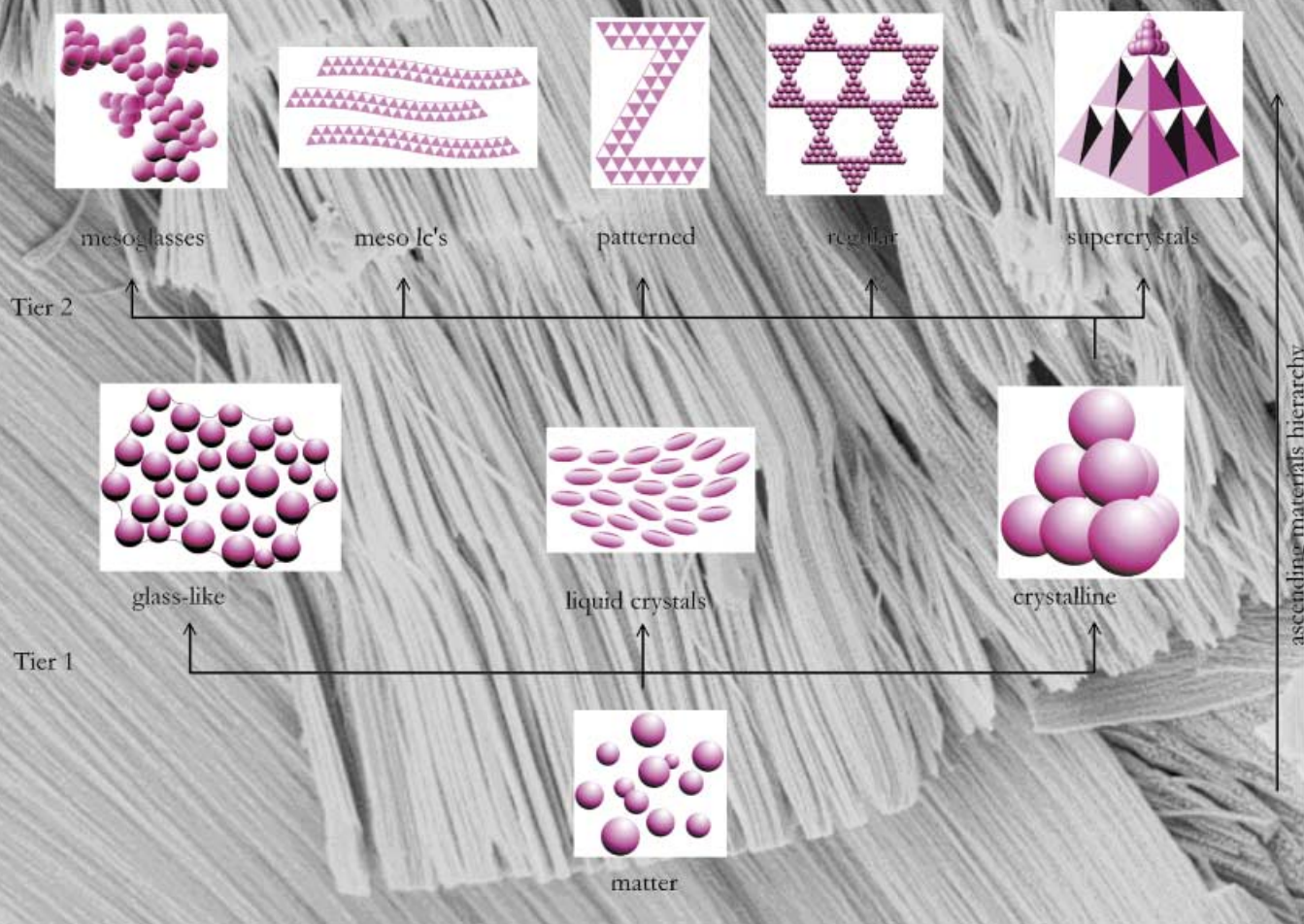
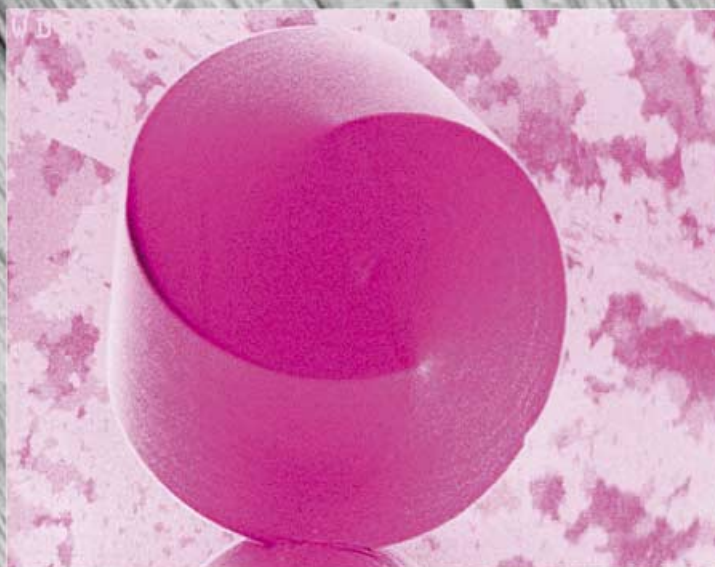


Why Meso?



Promises and Problems of Mesoscale Materials Chemistry or Why Meso?

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Abstract: Manipulation and control of chemical structures on the mesoscale has recently developed to a very promising and also aesthetically appealing area of chemistry. This concept article tries to integrate the views of two experts to delineate the specific principles, approaches, and the novel opportunities for chemistry that arise from the rational control of matter and functionality on that scale.

Keywords: crystal engineering • hierarchy • materials science • mesoscale • pattern recognition • self-assembly

Introduction and Definitions

In our time, “nano-” and “meso-”-words have left the science reservation and entered the public and political perception. Indeed, bulk materials can be remodeled as nanomaterials in two main ways through bottom-up chemistry and top-down engineering-physics strategies: the first by reducing one of their physical dimensions to the nanoscale and the second by providing them with nanoscale porosity. When talking about finely divided forms of bulk matter, nanomaterials characteristically exhibit physical and chemical properties different from the bulk, as a consequence of their having at least one spatial dimension in the size range of 1–100 nm. Nowhere is this better illustrated than in the emerging area of nanoclusters or quantum-dots^[1] and nanowires.^[2]

Solid-state properties, such as melting point and conductivity, show a strong dependence on the scale of some nanometers; this has turned out to be relevant for nanotechnology real devices and applications.

If we have “nano”, what is “meso”? Care has to be exercised when asking this question. It is well known that different materials properties, defined by physicochemical underlying principles, scale with the physical size with distinct length scales in the meso region. Therefore, meso can mean different things.

For instance, the International Union of Pure and Applied Chemistry has imposed length scales on three different ranges of porous materials, microporous <2 nm, mesoporous 2–50 nm, macroporous >50 nm, whereby these designations strictly refer to the pore sizes and not the dimensions of the material between pores.^[3] So pore length scales are set by a convention and in this context the mesoscale is clearly intermediate between that of the microscale and macroscale with no mention ever of nano when it comes to pore dimensions. Meso is, however, only defined by a scale.

In soft matter science, again mesophases are ubiquitous and become entangled in a scale of complexity when utilized as structure-directing templates for making hard mesostructured forms of matter.^[4] Again, “nano” is not mentioned, and “meso” extends over a wider size range as for the porous systems, say 2–500 nm. The nano-size, however, is just a side aspect, as a mesophase is classified by its order and its mode of self-organization.

Our understanding of “meso” follows this model: “meso” is not directly related to a length scale, but to a principle of operation: it is “in-between”, that is, in-between molecular and solid-state chemistry, in-between a molecular and a continuum approach, in-between covalent chemistry and micro-mechanical techniques. It is where new and exciting science is happening, which cannot be pre-described by laws on the scale of atoms and molecules alone. It will turn out throughout this article that this is much more than to be expected by a scale alone, that is, “nano”, and this is why we use the notation “meso” throughout the next.

As this is semantics only, we prefer to move directly to the scientifically and technologically more relevant question of: “why meso”? Mesostructured materials can be nowadays routinely accessed, for instance with the right kind of supra-

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molecular approach by means of soft matter templates. It is not the purpose of the present article to review and delineate the different tools that have been recently developed to perform materials chemistry on the mesoscale. There is already a number of papers and reviews that have described (e.g., references [5–8]) in detail how diverse kinds of soft matter can self-organize into different mesophases, and that these mesophases can act as templates for creating replicates made of hard matter, encompassing, for example, the classical solid-state library of metals, semiconductors, insulators, and nanoclusters, as well as soft matter agglomerates and polymers thereof. After about ten years of intense activity in the field of making mesoscale matter, one can only say that synthetic strategies to a wide composition and structure field are more-or-less under control, and that some idea of property–function relations are emerging. On the other hand, utility is still rather lacking, and the invention of mesoporous solids, for instance, has led to intense research activity measured in thousands of papers, but not to a single real application.

This is why we want to critically examine the evidence and try to address the question if there is anything unique about mesoscale materials chemistry, revealing essentially not some type of photograph of all the details, but a schematic roadmap of the field. By advancing, we will hopefully identify the peculiarities and promises of the field, but also try to mark some of the popular illusions and misunderstandings.

The Tasks of Mesoscale Chemistry

Mesoscale chemistry can be defined at first as the controlled generation of objects with characteristic features on the mesoscale with chemical reactions and principles (“tools”) specific for this level of molecular assembly. It is not classical covalent chemistry to be applied on meso-objects, but rather includes routes and chemical strategies especially designed to be effective in the nano- and micro-range. Mesochemistry bridges the world of molecules connected by molecular bonds and the chemical engineering of micron-sized structures (the lower end of the macro-world), such as lithography, chemical vapor deposition, or coating techniques.^[9] It will turn out that “meso” is indeed “in-between”, both in-between the lines, fields, and the limits of the currently “make-able”.

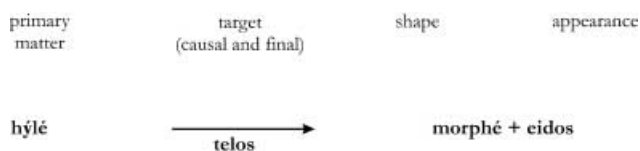
Chemistry is the art of manipulating bonds, interactions, and arrangements of atoms, groups, and components in a controlled and reproducible fashion. But in the context of the mesoscale, what can be meant by control?

- 1) Size, shape (the habitus), surface area, and curvature are definitely something a chemist wants to control for meso-components such as hybrids, composites, and porous systems.
- 2) Surface and interfacial chemistry, and texture (e.g., glassy, nanocrystalline, crystalline-like) are heirs from the solid-state chemistry side, and are also key aspects to control.

- 3) Mutual arrangement, morphology (from *morphé*: shape or contour) and order are something more specific for the mesoscale, as mesoscale structure can be orchestrated from a completely disordered to a partially ordered to a completely ordered state of matter. The morphology of mesoscale matter can be arranged through various chemical and physical strategies to be finely divided particulate, fiber, film, monolith, sphere, superlattice and patterned forms.

This gave rise to the notation “morphosynthesis”,^[10] which nicely catches the newly emerged possibility to synthesize/control a “*morphé*”, with all the possibilities for material science coupled to that.

It is appealing that modern chemistry returns with such concepts to the very roots of its foundation. Aristoteles defined “physics”, with a biological undertone, as the phenomenon that all matter is driven to adopt a form and an appearance (Scheme 1).



Scheme 1. Picture of Aristoteles’ “physics”.

This concept goes well beyond the simple control of purity and composition and is by its very core modern and embodies the spirit of morphosynthesis. Note that classical molecular and solid-state chemistry can be used to design a specific geometry, but cannot provide a variation of morphology nor curvature of a given structure. This is already a first answer to “why meso?”.

- 4) Last, but not least, it is highly desirable to control topological defects. Defects are mostly misunderstood as the “impurities” of mesoscale chemistry, and just as there is no pure organic compound, there is no defect-free mesoscale system. In fact, defects are not just impurities, as they can have a quite strong influence on the shape and morphology of a mesosystem, and a “chemistry of defects” (=rational control of defects) might turn into a very powerful tool in materials chemistry as a whole. Defects in mesoscale hard matter cannot yet be regarded as being under control. These defects are not just of the classical solid-state intrinsic microscale point, line, and planar kind, which are thermally populated (with a Boltzmann distribution) and abound in the mesostructure, there are also controlled structures of higher energy, which play a significant role in growth and form; they may block diffusion pathways in low-dimensional systems and can act as killer traps for charge carriers and photons.

The Importance of Mesoperiodicity and Mesoregularity; Structural Features beyond “Glasslike” and “Crystalline”

With this list of control options, it becomes evident that the chemical approach towards such objects has to address at least two levels or tiers at the same time; on a molecular scale, it is still the crystalline, glassy-disordered, or nanocrystalline structure that is responsible for the properties of the system, but on the mesoscale, the hybrid structure or porous system can adopt a “glassy-disordered”, grain-boundary-controlled nanocrystalline or perfectly periodic, crystalline-like texture again. There are examples of periodic mesostructures formed from a molecularly crystal-like organic component integrated into a molecularly glassy inorganic material.^[11]

Because of these various ways of organizing matter at the mesoscale, one needs to be alert as to how this intermediate length scale can affect the materials properties. Such order parameters not only influence magnetic behavior, electron transport, the competition between radiative and nonradiative processes, but also have an impact on how one needs to think about their mechanical properties at the mesoscale, as well as mass transport and diffusion behavior of gases and liquids in confined mesoscale spaces. Figure 1 depicts some of the modes of organization we are allowed to expect by combination of order on the molecular and meso tiers.

Examples for mesoglasses are the condensed cluster hybrids by Schubert or Sanchez, et al.;^[12,13] examples for mesocrystals (crystals of nanocrystals) were reported by Rogach, Talapin, et al.^[14] and by Liu, et al.^[15] In addition, the order at the mesoscale is not just restricted to be strictly periodic or random, but it can also adopt a myriad of other structural motifs; for instance, it can be patterned and regular beyond the unit cell. Such structures simply cannot be realized on a molecular scale due to energetic reasons (as argued above).

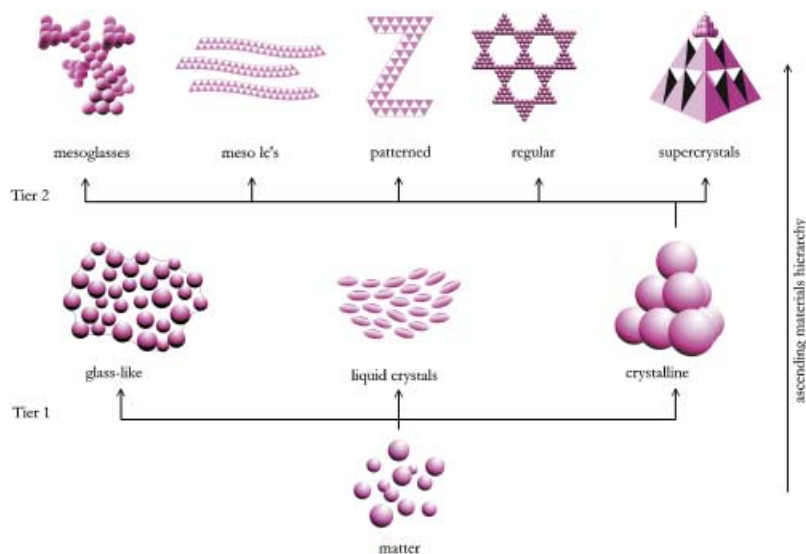


Figure 1. “Order on different scales”: matter can form liquid or glass-like, liquid crystalline or crystalline material. On the mesoscale, all three elemental order principles can reoccur, for example, there is a “crystal-of-crystals”. In addition, regular noncrystalline and patterned arrangements can be made.

A valid question is, therefore, when do we need a mesostructure to have periodic properties and when would a random one be preferred? Also, when does the dimensionality and orientation of the mesostructure influence the relationship between structure and composition, and property and function, which ultimately can impact upon utility through the electronic structure, optical, magnetic, and electrical properties.

Regularity with respect to the meso-object size (but not the mutual arrangement) has always an advantage when a model character or a sharp onset of a physical effect is demanded. This is true for all size-dependent effects, such as the quantum size effect in spectroscopy, excitonic properties, or the onset of gas adsorption. Such systems have just one onset point, just one size to calculate with, just one single site for catalysis, providing a certain clearness of argument and understanding.

Regularity with respect to packing (involving potentially more than one size or even a size distribution, as in foams) gives the maximal space filling with a minimal surface area involved; for example, cubic structures give the maximal space filling with minimal surface areas of spheres, hexagonal packing does the same for rods. As Nature in most cases tends towards maximal structural density (= optimization of attractive dispersion forces and cohesion energy) and minimal interfaces (= minimization of interface energy), those structures are most stable and allow for the maximal effect in a minimal volume.

A similar argument should hold for the mechanical stability and performance of such mesostructured materials: regular foams with constant wall or pillar thickness show superb material properties per gram of material;^[16] as it was also pointed out in a recent article on the mechanics of mesostructures,^[17] the honeycomb structure provides maximal stiffness from wax with minimal material, and wood and bone are mesostructured cellular materials with uncommon meso-

order (Figure 2).^[18] To simplify a longer story, constructions have to be regular (but not necessarily periodic, see Figure 1), and so do mesostructured objects if they have to fulfill certain mechanical expectations. Regularity, however, does not mean strict long-range translational order, as cellular, foam-like structures show comparable and partly superior performance. The behavior of regular structures opposes the so-called aerogels, which are fractal or statistical networks in which the mechanical stress just goes through certain gel strands, whereas others do not contribute at all. This lowers the mechanical performance by several orders of magnitude.

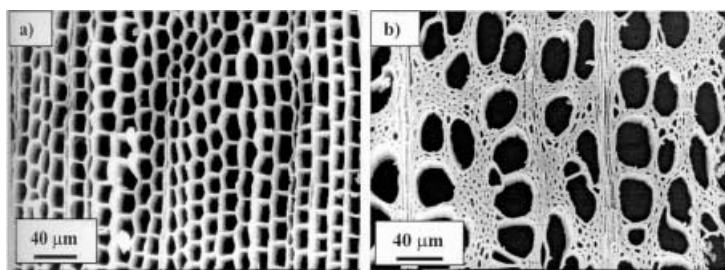


Figure 2. Cellular structure of wood: a) regular structure of pine wood; b) hierarchical pore structure of beech wood, an evolutionary more progressed species. Adapted from references [19,20].

As both regularity and periodicity give a maximal structural density with minimal surface area, it is exactly not what you want for surface-based applications in porous systems, for example, if one looks for maximal adsorption area or catalytic activity. A maximal structural density also gives high back pressure, and makes all flow and transport through the structure limited (diffusion or Knudsen transport), which is impracticable for application. This was well caught by Rolison in a very nice recent review article^[21] about the “unimportance of regularity” for catalytic nanostructures. Both restrictions of surface area and back pressure are, however, no problem for meso-order, as other modes of organization with high surface area and high flow-through permeability can be implemented. Sponges, for instance, have optimized their living structure according to surface area and ease of transport, and there is an analogue of their hierarchical, noncrystalline but not disordered pore structure on the mesoscale, for instance in high-performance chromatographic beads and separation gels.^[22] Similar performance optimizations were recently accomplished by foamlike, bimodal pore structures.^[23] It must be noted that in addition hierarchical pore systems allow much higher overall porosities (easily up to 90–95%) than “crystal-like” systems, while preserving the structural integrity.

Regularity of structural units and of their mutual arrangement, however, can lead to the occurrence of the most exciting meso-effects (opals, colloidal crystals, photonic crystals). Here, because of superb periodicity, “coherent” effects evolve, for example, Bragg scattering in the optical range or the development of photonic band gaps.^[24,25] Bragg’s law is a good tutorial on the sensitivity of the coherent effects on defects. Debye–Waller type disorder, that is, positional disorder with a Gaussian distribution, will damp the peaks, a distribution of objects with positional precision leaves all peaks intact, but gives a coherent structured background, and site-defects serve only to lower the peaks and add an incoherent background.

The understanding of the influence of changes of the mesostructure on the optical properties is important for using regularity for sensing (e.g., the construction of a Bragg or photonic sensor). This sensor will be especially sensitive where the change (refractive index by chemical sensing, effective wall thickness by regular adsorption) influences a zero transition, that is, at the band gap or point of destructive interference. In this mode, a change of all sites is required, as these are coherent effects. If a single pore is

changed, for example, by the binding of a single big molecule or deformation through a cell, the incoherence is increased, and the signal is best seen at the point of maximal constructive interference, that is, at the maximum of the Bragg peak. At this point, the meso-arrangement expresses by its color what is felt in a single pore.

A complete swelling of such a structure due to an outer stimulus is obtained for so-called “p-inks”,^[26] whereby an electroactive polymer changes its color when put under the appropriate voltage. This can become useful for addressable, large, colored screen plate applications.

Going from the very regular to less regular structures, it is to be stated that meso-analytical methods becomes very demanding, as neither microscopic nor macroscopic techniques are really suitable, and new techniques, such as GISAXS (grazing incidence small angle X-ray scattering), have to be developed or improved. Also the assessment of mechanical properties and the development of a compound theory on this scale (“mesomechanics”) is at the best an open question, as continuum properties cannot be extrapolated towards this scale, and the outcome of these assessments will influence future applications for mesomaterials, for example, in microelectronic packaging and electroactive devices like fuel cells, solar cells, batteries, and sensors.

The Explosion of Complexity, the Entry of Curvature and the Role of Nuclei and Defects

It already became evident that mesoscale structures are richer than molecular structures; in addition to crystalline and glassy structures, we can also find partly ordered structures, the patterned coexistence of different types of order, hierarchical and scale invariant order, and so forth. Due to increased complexity of the energy hypersurface and the role of slowed-down kinetics, metastability of different structures gains importance, much more can be made. Here, chemistry develops conceptual similarities towards art, an analogy recently pointed out by Lehn.^[27] Also living Nature can handle structural metastability in its most impressive form. In one or the other sense, mesoscale chemistry is, to a large extent, doomed to reinvent nature, with the only justification and hope being to extend it to other materials bases and new, evolutionary not yet invented principles. This “explosion” of structural complexity is presumably the most important answer to “why meso?”.

For instance, curved objects can be synthesized, either by a rational control of noncrystalline self-assembly^[28] or by the interplay of defect-design and complex soft-matter order.^[29] In the latter case, nanomeso is not just “games with words”, because nanoscale mesostructures do exist. The nanoscopic nuclei of mesostructures can, for example, be captured by quenching the early stages of the surfactant-templated assembly of mesoporous silica,^[30] or they can be trapped by evaporation-induced self-assembly of surfactants and silicates within the spatial confines of aerosol nanodroplets.^[31] The growth of siliceous mesostructures begins with the formation of a seed, a co-assembly of surfactants and silicates; however, what is special about this meso situation is the

nature and temporal evolution of the “viable nucleus” that is initially created from the synthesis nutrients. In the “incubation” of the seed “soft silicotropic matter” is generated whose order and shape is dictated not by crystallographic physics, space groups, and the underlying symmetry of a rigid unit cell that creates platonic form, but rather shape is determined by a nanoscale deformable mesophase that assumes a form predicated instead by the theory of elasticity. The critical size of such an elastically deformable, ordered nucleus, which is able to sustain growth rather than simply re-dissolve, is governed by the equality of surface and bulk free energy. This soft seed appears to be around 50 nm in size, and, interestingly, can be an association of about ten surfactant aggregates in each direction or order.^[32,33]

The structure of this nanomeso unit as well as the evolution of this kind of complex soft matter nucleus in time is of special interest, because it is expected to involve a rather complex interplay of subtle factors, each of which can have a profound effect on the final form. Not a great deal is currently understood about this important aspect of morphogenesis with its biosilicification connotations. From the little knowledge that does exist, it is clear that growth is intimately connected to colloidal interactions (electrical double-layer repulsion and van der Waals attraction forces) operating between the evolving seed and the accreting surfactant–silicate micelles for the particular choice of synthesis conditions (ionic strength, dielectric constant, temperature). It is also apparent that topological defects of particular strength form within the emerging nanoscale mesophase, driving it to assume a specific internal structure and shape that depends on the synthesis conditions as well as surface and bulk elastic free energy.^[34] It is this intricate interplay of colloidal and elastic forces that lead to the mesostructure organization and impressive “biomimetic” silicified curved shapes (rods, gyroids, toroids, spirals, and spheres) observed for mesoporous silica and organosilica materials templated by surfactant micelles (see Figure 3, reproduced with permission from references [32,33,35]).

Another unusual aspect of this growth process is the gradual rigidification, induced by hydrolytic polycondensation of a silicotropic mesophases. This too is a complex topic and much remains to be learned about the details. What is currently known is that polymerization of silicate species in an emerging silicotropic nanomesophase leads to contraction-induced stresses in the mesostructure; this results in fasci-

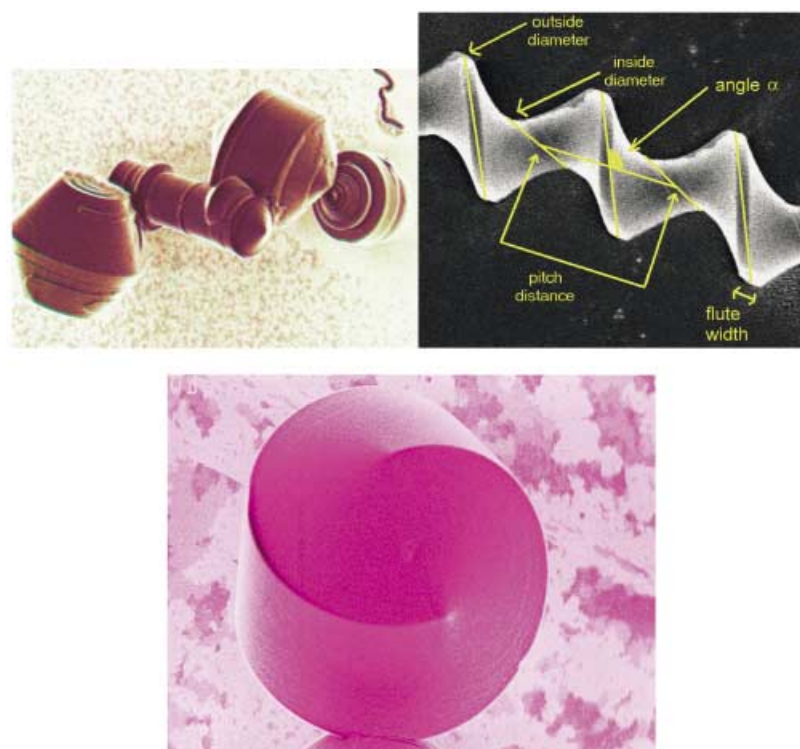


Figure 3. Various morphologies of mesoporous silica, made by morphosynthesis and defect design.

nating buckling patterns observed on mesoporous silica curved forms (Figure 4). The design of these buckling patterns is related to the organization of the mesostructure and the anisotropy of contraction-induced stresses within the curved form. Curved patterned shapes are definitely a distinctive feature of meso.^[36]

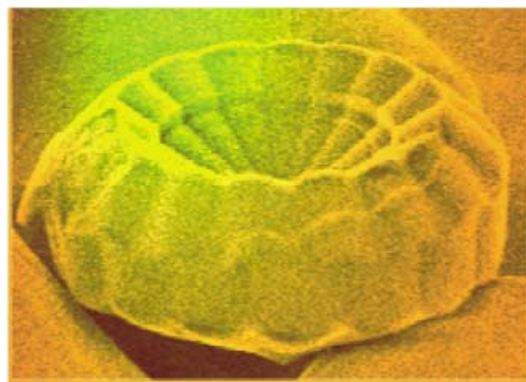


Figure 4. Buckling patterns in mesofilms and objects.

If Molecules Are Substituted by Components, What Is Mesobonding?

The question of mesospecific binding operations has to be briefly discussed, as mesochemistry has the potential to join very different nano- and mesostructures with linkages beyond the covalent bond. As binding between larger units

is complex and involves a number of bonds, it cannot be performed by statistical means, that is, without control. Simple heat-and-beat chemistry will not work, as we cannot separate the side reactions from the correct connections, and undesired ill-posed structures or statistical aggregates would be obtained. To avoid that, essentially three different meso-binding techniques are employed:

- 1) Self assembly and reversible binding.
- 2) Template techniques.
- 3) Employment of physical binding, such as adaptation of cohesion energy by adhesion layers or electrostatic binding layers.

Self-assembly is the mutual arrangement of components by optimization of intermolecular potentials in a geometrically controlled fashion. It is, by its *modus operandi*, reversible, that is, only the typical secondary interactions of supramolecular chemistry (e.g., hydrogen bridges, ligand binding, amphiphilicity, some Coulomb binding) can be employed. Again, by its very definition, the overall binding energy must be of the order of some kT (say 8–10 kT), as the bond must be sufficiently strong, but must have a certain probability to be “open” for self-optimization and self-repair.^[6,27] Self-assembly is an integral part of many mesochemical operations.

Template techniques also work for the stronger and irreversible covalent and ionic binding. A reaction is mesostructurally directed by the fact that it is simply geometrically expelled from some compartments in space by regular fill-ins or directed along outer forms.

If two different meso-objects cannot bind by their very chemical nature, they can be “glued” together by adhesion layers. This technique—well known in the macroscopic world—can be brought down to the mesoscale, thus creating chemically very unusual heterojoints. Here, we want to point to the work of Decher and Möhwal, ^[37,38] Mallouk, ^[39] Kotov, ^[40] and Caruso, ^[41] who organized oppositely charged polymers, clusters, and biopolymers with diverse composition and functions, by electrostatic gluing in a layer-by-layer fashion to create designer mesoscale films on planar and curved surfaces, thereby providing exciting opportunities that cross the boundaries between most areas of materials science.

Binding of micro- to millimeter sized objects by adaptation of surface free energies, the coupled lateral capillary forces, and shape recognition was employed by Whitesides et al.^[42,43] Here, a certain “reversibility” and self-optimization was ensured by mechanical agitation, which takes the role of thermal energy for larger objects. In another paper, the same group provided the assembling system with functions, that is, conductive wires and photodiodes, and the whole structure was functional.^[44]

The last example nicely illustrates that on the mesoscale, the notation “bonding” slowly transforms into “interfacing” (analogue to its engineering sense), as not only the mechanical connection by binding between the chemical components has to be addressed (the physical plugging), but also the exchange of functionality, electrons, or information (the wiring

of the interface) has to be pre-described by chemical means. This is not only true for the macroscopic world as in the Whitesides’ example, but goes down to nanometer-sized structures whereby effective charge separation and transfer between different components has to be encoded by band-gap engineering.

Epitaxy, Mesoepitaxy, and Pattern Recognition

The concept of mesoepitaxy is a related issue that introduces some unique features on the mesoscale. In the semiconductor chemistry and physics of planar electronic and optical devices, epitaxy, the matching of the lattice dimensions of two crystalline solid-state materials at an interface, is a pivotal consideration for controlling the properties and efficacy of junction devices. There is a certain tolerance of lattice mismatch that is permitted before elastic strain at the interface creates defects of various kinds that can scatter and trap charge carriers and photons, which degrades the performance of the device. Such lattice mismatches can be utilized to advantage for the physics-type self-assembly of quantum nanostructures through the controlled development and patterned release of strain in heteroepitaxial junctions. A valid question, therefore, is what about matching materials properties at the mesoscale beyond that of simply atomic and molecular lattice dimensions, but to include phenomena at supramolecular scales?

Here, again the aspect of increased metastability and the rather soft potentials involved come into play, which makes “mesoepitaxy” a broader and more general phenomenon. In fact there is growing evidence in the literature that mesoepitaxial phenomena do indeed exist and have a major influence in the way that a mesophase interacts with single-crystal surfaces like mica, graphite, and silicon, and that is distinct in behavior to the way it interacts with randomly structured surfaces like glassy silica and polymers. Because many materials structured at the mesoscale are grown as films on planar substrates, to achieve a particular property the structure, surface charge, hydrophobicity, or chemical functionality of the underlying substrate plays a special role in the nucleation, growth, orientation, and form of the mesostructure.^[45,46]

Mesoepitaxial effects are seen in the preferred orientation of hard mesoscale thin-film materials replicated from a soft mesophase. The constituents of the mesophase clearly interact in a specific way with particular surface sites and may organize with a preferred orientation on the substrate. In fact even defects can in principle be eliminated and/or controlled by careful selection of the structure and surface properties of the substrate as well as with chemical patterning techniques, for example, self-assembled monolayers (SAMs). A particularly nice example for the intelligent use of mesoepitaxy in material science is the orientation of self-organizing discotic semiconductors along directionally coated polytetrafluoroethylene-coated surfaces and the coupled increase of electron conductivity.^[47]

In this context it is interesting to contemplate the idea of creating hetero-mesoepitaxial junctions between mesoscale

components with intentional mismatch of the lattice dimensions at the interface. In this way it should be possible to induce elastic instabilities in one or both of the mesoscale components; it is these instabilities that drive the formation of patterns at a length scale determined by the bulk and interfacial free energies of the system. Indeed buckling patterns have been observed in hard mesostructures arising from differential, polymerization-induced, contraction stresses in an elastically deformable soft mesophase as it gradually transforms to the hard replica material.^[36]

It is important to denote that “epitaxy” on the mesoscale can be part of a much broader notation, namely pattern recognition. As we not only have access to periodic-crystalline and glassy-disordered arrangements, but also to other regular and patterned structures, the interaction of objects can be encoded in much finer detail than by classical epitaxy or by the simple adjustment of polarity.

Figure 5 illustrates this statement. If “grey” and “white” denote two states of a surface whereby grey–grey or white–white is bonding and grey–white is antibonding (e.g., hydrophilic and hydrophobic spots of a surface), it is only those patterns with similar periodicity and geometry that will bind to each other, whereas all others do not sum up to an over-

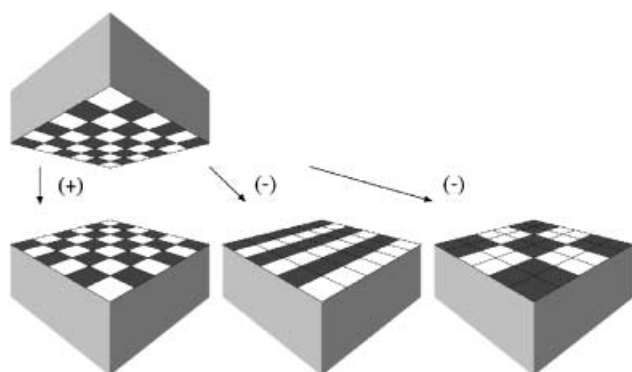


Figure 5. Illustration of the principle of pattern recognition. Assuming the “like” of similar colors and the “dislike” of different colors, the patterned surface on top will only bind to its counterpart on the left, but not to the others, in spite of their apparent similarity.

all binding situation. That way, a large multiplicity of mutually recognizing surfaces can be made, giving rise to addressed hetero-assembly towards very complex objects by the rational choice of surface structures.

Such pattern recognition is “error-tolerant”, because the degree of binding is proportional to the “similarity” of the two patterns (defined by the convolution integral), so related patterns or patterns with site defects are also recognized. This error tolerance is again a specific meso feature, as a sum over many secondary interactions can be employed. By similar arguments, it also becomes clear that patterns involving structural or compositional gradients allow a mutual positioning with nanometer precision^[48] or make objects moving “uphill”.^[49] These surface structures can be created by microstamping, but also by lithographic techniques combined with subsequent chemical reactions. There are also certain indications that such a recognition of natural pat-

terns play a role in the highly selective, mutual alignment of polymer- or ligand-coated nanocrystals towards mesohybrids,^[50] partly with curvature and complex form.^[51,52]

The work of Mallouk presents a fine and imaginative variety of pattern recognition on objects, including the self-assembly of “bar-coded” nanowires into mesoscale agglomerates with predetermined geometry for logical and memory circuit applications,^[53] as well as nanorod mesophases from selective surface functionalization of barcoded nanorods.^[54]

The rational access to and the use of pattern recognition for the controlled assembly and mutual positioning of meso-objects is definitely another point on our “why meso?” list.

Mesoprinting with Stamps and Tips

Since the discovery that alkanethiols self-assemble on gold to form well-ordered monolayers and that alkanethiols can be faithfully transferred from a patterned elastomeric polydimethylsiloxane (PDMS) stamp to a gold substrate, termed microcontact printing,^[55] to form replica patterns at the 10000–100 nm scale, there has been a determined effort to reduce the print scale to below 100 nm. The opportunities for organizing matter at the sub-100 nm scale include making metal contacts sufficiently minute for electrical connections to molecules and polymers in electronic devices; to create nanocluster and nanowire electronic, photonic, and sensory circuits; and to assemble nanocrystal and nanorod arrays for biodiagnostics.

In the last few years, major strides have been made towards the realization of practical ways to perform mesocontact printing. One such strategy utilizes mesoscale defect patterns intentionally designed in SAMs.^[56,57] These defects form spontaneously at metal interfaces created, for example, by a nanoscale thick film of Ag deposited on a Au substrate, and are found to promote nucleation and growth of materials like calcium carbonate with respect to ordered regions of the SAM. Defects in SAMs have also been found less protective as etch resists on gold than ordered regions of the SAM. Patterning mesoscale disorder in SAM resists, called topologically directed etching, enables patterning of the underlying substrate with sub-100 nm structures.

Mesoscale patterns of SAMs an order of magnitude smaller has been achieved by directly writing alkanethiols on Au by using the fine tip of a scanning probe microscope.^[58] By chemically matching the ink to be printed with the surface chemistry of the substrate, it has proven feasible to directly write patterns as fine as 10 nm of a variety of molecules, polymers, biomolecules,^[59] and materials on disparate substrates like metals, semiconductors, and dielectric materials.

Impressively small features have recently been achieved through the combined use of V-shaped sharp and hard PDMS stamps in which the contact area is below 50 nm and high-molecular-weight dendrimer inks are employed to avoid diffusive smearing of the patterns.^[60] Unlike printing mesoscale patterns with the tip of a scanning probe microscope in a sequential writing mode,^[61] the mesocontact printing method enables the patterning of large areas of substrates simultaneously, and it is anticipated that the use of

higher density V-stamps with features below 10 nm will facilitate single molecule, single-strand polymer, or protein patterns to be deposited.

Armed with these straightforward protocols for performing top-down chemical patterning of mesoscale features and the self-assembly chemistry methods described earlier, the floodgates are now open wide to address a large number of unanswered questions and problems in mesoscience. Directed self-assembly strategies that fuse mesoscale patterning with self-assembly, provide a straightforward means of organizing and connecting molecules, polymers, and materials into integrated chemical, physical, and biological systems with a purpose.^[62]

Case Studies: Some Selected Applications of Mesoscale Materials and Their Promises

Let us return to the original question of why mesoscale materials and what is unique about this intermediate state of matter? It is clear from the last decade or so of research by polymer and materials chemists that they have recognized the opportunity now exists to remodel the periodic table of known compositions into materials fashioned at the mesoscale. New mesoscale materials appear daily in the literature. It is important, therefore, to appraise some of the "early" accomplishments of mesochemistry to try to identify promising future directions for science and technology for these intermediate length materials.

Low-*k* dielectrics: Low-*k* dielectrics are important as packaging materials for future developments of smaller, more densely packed, and faster microelectronics. Thin-film dense silica has always been the material of choice for this application and is likely to remain dominant in this role, because its dielectric constant can be further reduced to meet electronic-device-scaling law demands by introducing porosity at the mesoscale and functional diversity by integrating organic groups into the structure.^[63] This is a classic case where the mesoscale can offer a unique combination of advantages not possible at other length scales.

Judicious choice of mesoscale organic templates, synthesis conditions, integration of terminal or bridge-bonded organic functional groups into the silica, and post-synthetic processing can provide a mesoporous organosilica film with a pore architecture that is simultaneously able to keep out water, minimize electromigration from metal interconnects, provide mechanical stability, and deliver the desired low value of the dielectric constant needed to optimize the performance of a microelectronic circuit.^[64]

Metal-oxide-based gas sensors: Metal-oxide-based gas sensors are the most widely used solid-state devices for detecting gases in the environment and atmosphere, and for controlling and monitoring gases in combustion engines and industrial processes. The sensitivity of these kinds of sensors intimately depends on length scale of the active structural elements, as the overall response of the device relies on measurement of a change in surface conductivity. When the

Debye or space-charge depletion length of the metal oxide comprising the sensor is comparable to the scale at which the metal-oxide-active elements are structured, then all of the material is surface and all surface sites are able to participate in the detection of adsorbed gases. Tin oxide, often modified by doping and additives, remains the industrial material of choice for many sensing applications. When tin oxide is templated into a periodic lattice with mesoscale structural elements, then the sensitivity, selectivity, and reproducibility of the sensor can be engineered in a rational manner and the electrical response of such a structurally well-defined sensor can be quantitatively analyzed in terms of resistor network theory (Figure 6).^[65]

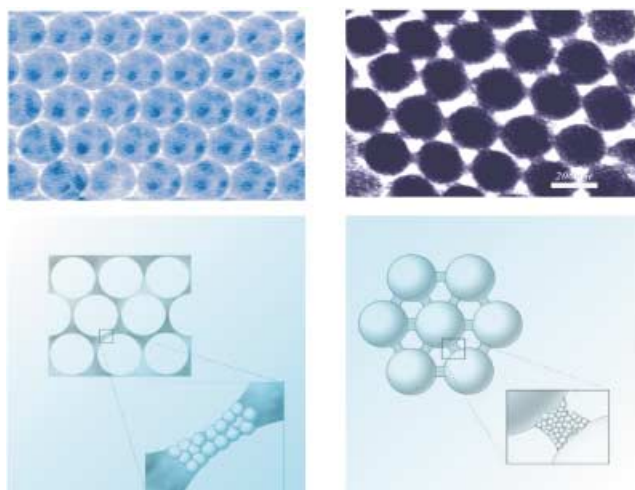


Figure 6. A SnO₂-opal and inverse-opal sensing array.

Solid-oxide fuel cells (SOFC): Solid-oxide fuel cells (SOFC) convert chemical to electrical energy. The solid-state materials that comprise the anode, cathode, and electrolyte components of the fuel cell must satisfy a number of stringent requirements for the efficient operation of the device. In an SOFC, a fuel is oxidized at the anode and oxygen is consumed at the cathode. Mesochemistry provides a unique opportunity to develop a new generation of SOFC materials that have mesoscale structural elements judiciously designed to optimize transport of fuel (hydrogen, methanol, alkanes) and oxygen into the electrodes, and their adsorption and reaction at active sites, while at the same time maximizing the mobility of oxide ions and electrons through electrode and electrolyte construction units in the cell. Mesoporous yttrium zirconium oxide or mesoporous cerium oxide anodes and a mesoporous lanthanum strontium manganate cathode constructed from nanocrystallites of these materials organized by a templating mesophase can achieve many of the requirements delineated above.^[66,67] An electrocatalyst based on metal nanoclusters of platinum or copper co-assembled with these anode materials provides the active site for chemical and electron-transfer reactions.

Following the arguments given above, nonperiodic hierarchical mesoporosity coupled with nanocrystallinity has the potential to enhance mass transport, ionic and electronic

mobility, and in particular maximize the three-phase-boundary length that controls the simultaneous contact between gaseous reactant, electrocatalyst, and electrode support, while at the same time retaining structural stability under the working conditions of the fuel cell.

Batteries, solar cells, and high-performance photocatalysts:

Batteries, solar cells, and high-performance photocatalysts will certainly represent rather soon new application fields of mesostructured materials. Nanocrystalline titania has been extensively studied for applications such as lithium rocking-chair-type batteries and solar cells. Electrochemical lithium insertion into nanocrystalline anatase is the basis of electrochromic devices and lithium secondary batteries. Also, nanocrystalline anatase is a promising material for dye-sensitized solar cells.^[68] Beside questions of optimized transport of charges and matter and the coupling of the space charges through the meso boundaries, the special electrochemistry and photoelectrochemistry of regular nanocrystalline or amorphous titania (which might be distinct to disordered forms of nanocrystalline titania) are “mesochemical” questions.

There exists a profound difference, for example, in the electrochemical and photoelectrochemical behavior of nanocrystalline titania and mesoporous titania with amorphous walls. Firstly, the electronic band gap of the latter is larger than the former; this most likely arises from quantum size effects and the amorphous nature of the thin channel walls of the mesoporous titania.^[69] Marked differences in the energy and distribution of surface and defect states were identified in photoelectrochemical and spectroelectrochemical experiments. For instance, in contrast to a nanocrystalline titania anode in a Graetzel-type solar cell, it is observed that mesoporous titania acted as a cathode. This is because of the smaller Fermi energy of mesoporous titania relative to nanocrystalline titania; this arises from the presence of many localized electronic states in close proximity to the HOMO of the dye-sensitizer and inefficient electron transfer in the thin amorphous channel walls.

Reiterating, it is an integral part of mesochemistry to impart “band-gap engineering” (or band-gap adaptation) and a controlled chemistry of surface sites; this is a must to control quantum efficiencies or increase light emission efficiencies. Recent work has for instance shown that surface engineering of CdWO₄ nanocrystals with polymer modifiers has made it possible to increase the photoluminescence of this scintillator material by a factor of two.^[70]

For the photochemical decomposition of chloroaromatic systems, a mesostructured titania scaffold has been constructed by membrane nanocoating (Figure 7); this again relies on a highly nanocrystalline anatase and the absence of surface defects.^[71] Such systems show at least as high photocatalytic activity as the industrially optimized nanoscale powder, but with the advantage of being a solid heterogeneous system with optimized flow-through properties (hierarchical pore architecture). Going from the directed homo-assembly of titania nanoparticles towards hetero-assembly with appropriate donor or acceptor nanoparticles (e.g., In₂O₃), it was possible to increase reactivity and make the

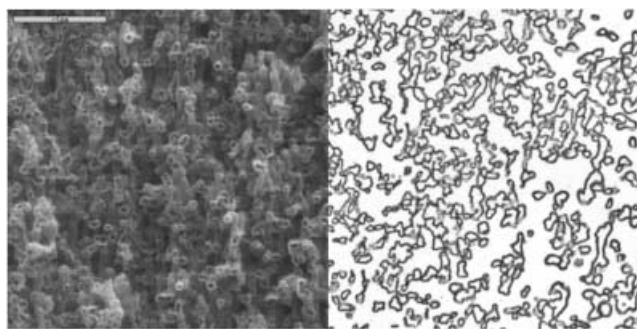


Figure 7. Mesostructured titania made by gel-coating; a) scanning electron micrograph, b) TEM of a microtomed slice of the same sample showing the high quality of nanoparticle alignment along the former template. The thickness of the single layers is between 30–50 nm.

catalyst operate in a much broader pH range relative to that of the industrial standard.^[72]

This type of heterojunction engineering, well known in semiconductor physics, is a rather new concept in colloid chemistry, introduced by Henglein et al. for the “attached colloid” pair CdS/ZnO.^[73] As mesochemistry also has the potential to join different mesostructures (not only atoms and groups) with linkages beyond the covalent bond, such an approach goes well with its generalized philosophy. This example also illustrates that “bonding” is a part of “interfacing”, as not only the mechanical connection between the single particles, but also the exchange of electrons and information has been chemically implemented by design. Clearly, mesochemistry also adds here a new level of complexity and potential.

Electrochromic devices and electronic ink: Electrochromic devices and electronic ink, known as E-Ink, is an exciting new display technology that exploits the coloring attributes of electrophoretics and electrochromic materials in a range of applications, such as at street, poster, and shop signs. To amplify on the latter class of E-Ink materials, a color change in an electrochromic material originates from a redox change in the active material. In order for an electrochromic material to function as a practical material in an E-Ink device, certain key requirements must be satisfied, especially a high color contrast between the two active redox states and fast switching speed. One illustrative system is a viologen-anchored nanocrystalline titania cathode in a solid-state thin-film electrochemical cell.^[74] Color response arises from a one electron, redox reversible reaction of surface-tethered viologen (V) V²⁺/V¹⁺ couple. The color contrast is related to the high surface area of the nanocrystalline titania support together with the associated large aerial density of V²⁺/V¹⁺ surface sites. Fast switching speed results from the favorable electron-transport properties of nanocrystalline titania and fast ion mobility of the charge-balancing lithium ion component of the electrolyte.^[75] Mesostructured electrochromic materials may offer advantages over existing materials due to the reasons discussed above.

Mesoporous materials: Mesoporous materials with controlled porosity and well-defined textures and morphologies are

expected to function as improved-performance stationary phases for separation processes. Because of the ability to template porosity at the mesoscale, for example, in a variety of inorganic materials, polymers, and carbon compounds, a unique opportunity presents itself to create a new generation of materials that may be cast as films for thin-layer chromatography or as separation membranes, as spheres for traditional chromatographic columns, as monoliths for high-speed chromatographic columns, and as micron scale elements for lab-on-chip analysis systems. The appeal of templated porous materials with regular structures that span multiple length scales is that they can be straightforwardly synthesized with particular pore sizes, tailored surface properties, and designed morphology. This can be rationally tuned through chemistry to provide optimum molecule adsorption and diffusion behavior that is reproducible from sample to sample, the goal being to maximize the resolution of chemical components of a mixture. It must, however, be repeated that a periodic mesopore structure has in general no specific advantage for chromatography or as a catalytic support,^[21] and in many cases periodic pore architectures are by principle coupled to serious disadvantages, such as non-optimal flow and surface area. This is one of the reasons why even after ten years there is still no serious application of MCM-type materials.

It is also to be underlined that current separation membranes or chromatographic beads already possess a mesostructured pore architecture, optimized by barely empirical means, for instance, by de-mixing effects throughout the solidification reaction (for a review of preparation techniques of such materials, see reference [76]). Any filtering relies on at least one homogeneous layer with the appropriate pores, but the smaller the pores, the thinner this layer has to be, as otherwise unacceptable backpressures would be built up. This is why standard filter membranes, which already exist down to the meso range, have a heterogeneous pore structure across the membrane. Adsorption chromatography rely on high interface area, which means very small pores, but also rapid flow through, which means very big pores. Here complex multimodal channel systems have to be implemented to fulfill both demands, which in addition have to be irregular over a long range, or else the plate number would decrease. There are a whole variety of techniques described to make such well-structured separation media,^[76-78] but rational approaches to design and implement channel systems with pre-described properties are still at the horizon.

Porous materials with mesoscopic dimensions also offer advantages as "mesocuvettes and mesoreactors", for example, as hosts for the synthesis and stabilization of semiconductor clusters whose size dependent properties only appear at the mesoscale. A good example concerns capped silicon clusters, whereby interesting quantum size effects, especially those relating to bright and fast visible photoluminescence and electroluminescence, only appear below the exciton size of bulk silicon, namely smaller than 5 nm, which falls in the mesoscale range of dimensions.^[79,80] To expand, recall that the search for a silicon-based light emitting diode (LED), which easily integrates with silicon microelectronics and has utility in optoelectronics or photonics, has inspired materials

research for more than a decade. Canham discovered that porous silicon made by electrochemical anodic oxidation of p⁺-doped silicon wafers could emit light when driven by photon and electron excitation.^[81] This initiated intense research activity in microfabrication and self-assembly approaches to different kinds of luminescent silicon structures suitable for LEDs. However, this has not proven to be an easy task, because a practical silicon-based LED must satisfy numerous stringent criteria, which include high quantum efficiency emission at room temperature with nanosecond radiative lifetimes; good charge-transport characteristics to facilitate effective electron-hole pair radiative recombination; long-term chemical, thermal, and mechanical stability; and a method of production that is straightforward, rapid, and cost-effective. Spin-on mesoporous silica films have provided a useful vehicle for enabling the chemical vapor deposition of disilane and growth of silicon clusters within the mesoscale channels of the film under extremely mild conditions.^[79] The silicon clusters display stable, room-temperature-visible photoluminescence and a radiative lifetime of eight nanoseconds. This procedure for making technologically interesting luminescent mesoscale forms of silicon bodes well for the future development of spin-on silicon-silica LEDs.

Another exciting application of silver clusters in mesoporous silica was recently described by Treguer-Delapierre et al.^[82] Synthesis of an Ag cluster in mesoporous silica films occurs for confinement reasons with a maximal density of silver nanoparticles. If such a film is filled with a liquid, practically all solute molecules are near to a silver cluster; this in turn gives rise to plasmon enhanced fluorescence or Raman spectroscopy. That way, such a mesostructured film with clusters acts as an optical amplification device, for example, to increase analytical sensitivity in very small liquid samples, and also carries the promise for nonlinear optical analytic materials.

Synthetic hybrid composite materials: Synthetic hybrid composite materials, in which organic and inorganic components are integrated by means of chemical, bottom-up, self-assembly approaches are also beginning to reveal certain advantages when fashioned at the mesoscale. Hybrid structures of this type are interesting as their properties can significantly transcend those of its component parts.

A well-known example for a natural pattern, which may serve as a biomimetic example for material synthesis, is that of the seashell, which is a layered mesohybrid of chitin and calcium carbonate and is 2000 times as tough as the constituent minerals.^[83] A simplified technical version was recently described with exfoliated and polymer swollen clays,^[84] whereby the addition of 5–15 wt% of clay to standard polymers, such as polyamides (nylon), significantly improved a whole range of mechanical parameters and resulted in an improved fire retardation.

Mesohybrid formation in the biomimetic sense is more than the existence of a microphase-separated product, as the added functional polymers lower surface energies and the interaction potentials of mesocrystals, thereby modifying the shape, orientation, and mutual alignment of the objects the

hybrid is constructed from.^[86] A particularly spectacular case are nanofibers: as (macro)fiber reinforced materials (e.g. carbon fiber) they are already omnipresent in high-tech applications and the potential of layered carbon-nanotube composites in the creation of a new generation of high-performance materials has already been proven.^[87,88] It is worth mentioning that the “mesotechnology” of polymer-modified crystallization (Figure 8) allows the extension of nanofiber composition from carbon to practically any crystalline system, for example, apatites^[89] and barium sulfate.^[34]

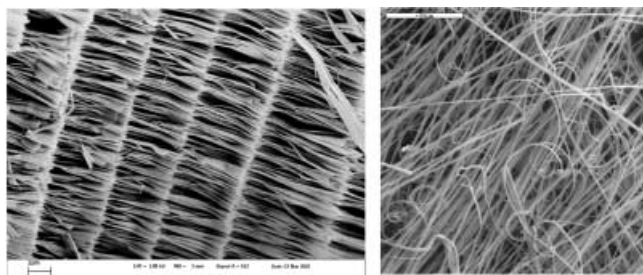


Figure 8. Examples of single crystalline fibers and fiber superstructures made by polymer-controlled crystallization. Adapted from reference [85].

Another recent example concerns hybrid materials called periodic mesoporous organosilicas (PMOs), in which a wide variety of bridging organic groups have been incorporated within the framework.^[90] By judicious selection of the organic group and the synthesis conditions it is possible to template PMOs in which the organic and silicate materials comprising the channel walls are either randomly oriented (glassy) or partially ordered, whereby just the organic constituent is oriented but the silicate is disordered (crystalline-like). There is great opportunity for this new class of meso-scale composite materials in a range of applications as diverse as chiral chromatography and microelectronics.

The Importance of Hierarchy: Meso Is Not Only the Next Step, but in Turn Leads to Further Steps

With the internalization of mesochemistry on top of classical chemistry, it became evident that such an integration is not an unitary event, but can be repeated on all length scales in a modular fashion,^[6] finally leading to hierarchically structured materials, such as bone and wood,^[18] and hierarchical chemical systems. Hierarchy is a defining feature of self-assembly that has long been appreciated in biology and is now emerging as a unique opportunity for making exciting new materials in chemistry. Hierarchy involves the organization of basic building entities in a serial or parallel, self-assembly, co-assembly, or directed-assembly process, whereby the process begins with the simplest construction units and assembles them into more complicated objects; assembly continues until the highest level of structural complexity in the hierarchy is attained. As the mesoscale is by its very nature

directly on top of the molecular scale it is uniquely placed in the hierarchy of materials structure and properties design considerations.

It was already stated that hierarchical construction of materials is omnipresent in nature, for example, wood and bone. Although made of rather simple and well accessible components, they show extraordinary, partly unparalleled material performances in the so-called Ashby plots;^[16] for example, the compression stability per gram of bone is four times higher than the one of steel. This makes the construction of hierarchical materials also appealing for purely synthetic materials.

A spectacular and rather appealing recent example for a three-stage encoding by chemical means only is illustrated by the surfactant-templated synthesis of periodic mesoporous benzenesilica, which displays order on three different length scales.^[11] At the molecule scale, incipient order is created through interaction between aromatic groups in the benzene silicate precursor. This ordering occurs simultaneously with ordering at the mesoscale, induced by the co-assembly of pre-organized benzenesilicate construction units with micellar templates. After hydrolytic polycondensation of the silicate moieties this results in hexagonal close-packed channels, whereby bridge-bound benzene groups are locked in an ordered state within a glassy matrix of silica. This process can evolve up to the overall macroscopic form of periodic mesoporous benzenesilica, the morphology of which can be curved and patterned in ways similar to those delineated above for mesoporous silica.

More general hierarchical structures in technology are inevitably made by a combination of bottom-up and top-down approach. Whereas the influence of processing and mechanical or electrical fields is strong on the macroscale, material chemists find themselves in the somewhat unfamiliar situation that they not only have to encode a hierarchy of interactions within the assembly behavior of the building blocks (nowadays up to three tiers by simultaneous encoding of different interactions), they also have to consider how to put their “structural reaction” under the correct outer stimuli. This is of key importance for the upper meso-range at which top-down and bottom-up approaches overlap.

To illustrate these ideas, soft lithography approaches have been devised that fuse methods of microcontact printing and micromolding together with a templating mesophase to provide micronscale patterns and shapes on planar and curved substrates like mesoporous silica. An example of this involves micronscale patterns of mesoporous silica, which integrates two levels of hierarchy in a single construct.^[91] A creative combination of latex colloidal crystal templating and micromolding in capillaries in unison with a templating mesophase is able to yield micronscale patterns of inverse colloidal crystals comprised of mesoporous silica, a strategy that in a single construct integrates three levels of hierarchy.^[92] Another case amalgamates micromolding in inverted polymer opal with a templating mesophase to create a mesoporous silica opal.^[93] Finally the process of crystallizing microspheres exclusively within spatially and geometrically pre-defined surface-relief patterns provides a novel route to colloidal photonic crystals with controlled area; thickness;

cross section and orientation; and high structural and optical quality (Figure 9).^[94,95]

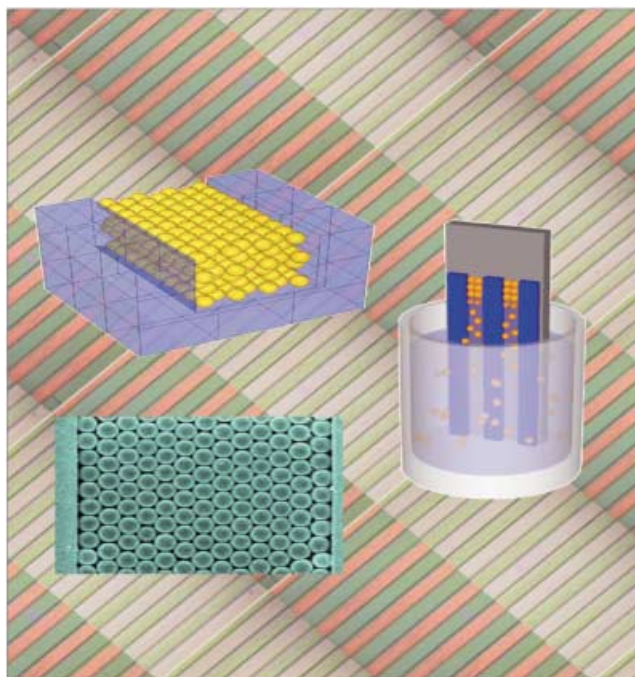


Figure 9. Construction of opal patterns with hierarchical structure by a combination of lithography, micromolding, and self-assembly.

The Pandemic Outlook: Gazing into the Mesoscale Crystal Ball

In the paragraphs presented above we have taken a brief, admittedly somewhat biased, yet critical look at mesoscale materials, past, present, and future, to try to appraise the original question is there is anything special about materials fashioned as this intermediate scale of matter. Some answers were given throughout the text, and the following list is just a short summary of some of the diverse options stated.

- Mesochemistry allows morphosynthesis.
- Mesochemistry accesses curvature for solid-state chemistry.
- Defect and nucleus design by chemistry.
- Adjustment of order between and beyond “glassy” and “crystalline”.
- Explosion of accessible complexity.
- Optimization of mechanical and transport properties by scaffolding and hierarchy.
- Design of “coherent effects”, for example, photonic crystals.
- Includes mesoepitaxy as a tool.
- Mesopatterns allow directed three-dimensional assembly and self-positioning.
- Error tolerance of binding and recognition.
- Design of meso-heterojunctions between nanoparticles.

- “Interfacing” on top of “bonding”, connection controls geometry and exchange of electrons, photons and stresses.
- Control of materials hierarchy by a combination of tecton layout and outer stimuli.

At this point in the development of mesoscale materials it is pertinent to ask whether mesochemistry should be considered as a distinct field of endeavor in the framework of materials chemistry? Does this approach have the potential to spawn new science and technology? At least we have evidence that attempts to make a case for the uniqueness of mesoscale matter indeed are adding previously unknown possibilities and techniques to the toolbox of chemistry. The answer to the questions posed above has to be left to the judgment and imagination of the reader. It will be interesting to watch the field unfold in the years ahead.

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- [1] H. Weller, *Angew. Chem.* **1993**, *105*, 43–55; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 41–53.
- [2] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353–389.
- [3] J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. Ramsay, K. S. W. Sing, K. K. Unger, *Pure Appl. Chem.* **1994**, *66*, 1739–1758.
- [4] S. Förster, M. Antonietti, *Adv. Mater.* **1998**, *10*, 195–217.
- [5] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319.
- [6] M. Antonietti, C. Göltner, *Angew. Chem.* **1997**, *109*, 944–964; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 910–928.
- [7] C. Sanchez, G. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chem. Mater.* **2001**, *13*, 3061–3083.
- [8] S. Polarz, B. Smarsly, *J. Nanosci. Nanotechnol.* **2002**, *2*, 581–612.
- [9] M. Antonietti, K. Landfester, Y. Mastai, *Isr. J. Chem.* **2001**, *41*, 1–5.
- [10] G. A. Ozin, *Acc. Chem. Res.* **1997**, *30*, 17–27.
- [11] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304–307.
- [12] U. Schubert, *Chem. Mater.* **2001**, *13*, 3487–3494.
- [13] F. Ribot, A. Lafuma, C. Eychenne-Baron, C. Sanchez, *Adv. Mater.* **2002**, *14*, 1496–1499.
- [14] A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase, H. Weller, *Adv. Funct. Mater.* **2002**, *12*, 653–664.
- [15] Z. R. R. Tian, J. Liu, J. A. Voigt, B. McKenzie, H. F. Xu, *Angew. Chem.* **2003**, *115*, 429–433; *Angew. Chem. Int. Ed.* **2003**, *42*, 413–417.
- [16] A. G. Evans, J. W. Hutchinson, M. F. Ashby, *Prog. Mater. Sci.* **1998**, *43*, 171–221.
- [17] A. M. Stoneham, J. H. Harding, *Nat. Mater.* **2003**, *2*, 77–83.
- [18] O. Paris, I. Zizak, H. Lichtenegger, P. Roschger, K. Klaushofer, P. Fratzl, *Cell. Mol. Biol.* **2000**, *46*, 993–1004.
- [19] P. Greil, T. Lifka, A. Kaindl, *J. Eur. Ceram. Soc.* **1998**, *18*, 1961–1973.
- [20] E. Vogli, H. Sieber, P. Greil, *J. Eur. Ceram. Soc.* **2002**, *22*, 2663–2668.
- [21] D. R. Rolison, *Science* **2003**, *299*, 1698–1701.

- [22] K. Lewandowski, F. Svec, J. M. J. Frechet, *J. Appl. Polym. Sci.* **1998**, *67*, 597–607.
- [23] M. Antonietti, B. Berton, C. Göltner, H.-P. Hentze, *Adv. Mater.* **1998**, *10*, 154–159.
- [24] S. John, J. Wang, *Phys. Rev. Lett.* **1990**, *64*, 2418–2421.
- [25] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, H. M. van Driel, *Nature* **2000**, *405*, 437–440.
- [26] A. C. Arsenault, H. Miguez, V. Kitaev, G. Ozin, O. Toader, I. Manners, *Adv. Mater.* **2003**, *15*, 503–507.
- [27] J. M. Lehn, *Supramolecular Chemistry*, 1st ed., Wiley-VCH, Weinheim, **1995**.
- [28] J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc. Faraday Trans.* **1976**, *72*, 1525.
- [29] H. Yang, N. Coombs, G. A. Ozin, *Nature* **1997**, *386*, 692.
- [30] S. Sadasivan, C. E. Fowler, D. Khushalani, S. Mann, *Angew. Chem.* **2002**, *114* 2255–2257; *Angew. Chem. Int. Ed.* **2002**, *41*, 2151–2153.
- [31] Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker, C. J. Brinker, *Nature* **1999**, *398*, 223–226.
- [32] G. A. Ozin, *Can. J. Chem.* **1999**, *77*, 2001–2014.
- [33] S. M. Yang, H. Yang, N. Coombs, I. Sokolov, C. T. Kresge, G. A. Ozin, *Adv. Mater.* **1999**, *11*, 52–55.
- [34] H. Yang, G. A. Ozin, C. T. Kresge, *Adv. Mater.* **1998**, *10*, 883–887.
- [35] S. Mann, G. A. Ozin, *Nature* **1996**, *382*, 313–318.
- [36] I. Sokolov, H. Yang, G. A. Ozin, C. T. Kresge, *Adv. Mater.* **1999**, *11*, 636–646.
- [37] Y. Lvov, G. Decher, H. Mohwald, *Langmuir* **1993**, *9*, 481–486.
- [38] G. Decher, J. D. Hong, J. Schmitt, *Thin Solid Films* **1992**, *210*, 831–835.
- [39] S. W. Keller, H. N. Kim, T. E. Mallouk, *J. Am. Chem. Soc.* **1994**, *116*, 8817–8818.
- [40] N. A. Kotov, I. Dekany, J. H. Fendler, *J. Phys. Chem.* **1995**, *99*, 13065–13069.
- [41] F. Caruso, R. A. Caruso, H. Mohwald, *Science* **1998**, *282*, 1111–1114.
- [42] N. Bowden, A. Terford, J. Carbeck, G. M. Whitesides, *Science* **1997**, *276*, 233–235.
- [43] A. Terfort, N. Bowden, G. M. Whitesides, *Nature* **1997**, *386*, 162–164.
- [44] D. H. Gracias, J. Tien, T. L. Breen, C. Hsu, G. M. Whitesides, *Science* **2000**, *289*, 1170–1172.
- [45] I. Sokolov, H. Yang, G. A. Ozin, G. S. Henderson, *Adv. Mater.* **1997**, *9*, 917.
- [46] H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *J. Mater. Chem.* **1997**, *7*, 1285–1290.
- [47] A. M. van de Craats, N. Stutzmann, O. Bunk, N. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus, R. H. Friend, *Adv. Mater.* **2003**, *15*, 495.
- [48] U. Srinivasan, D. Liepmann, R. T. Howe, *J. Microelectromech. Syst.* **2001**, *10*, 17–24.
- [49] M. K. Chaudhury, G. M. Whitesides, *Science* **1992**, *256*, 1539–1541.
- [50] Z. Y. Tang, N. A. Kotov, M. Giersig, *Science* **2002**, *297*, 237–240.
- [51] S.-H. Yu, H. Cölfen, M. Antonietti, *Chem. Eur. J.* **2002**, *8*, 2937–2945.
- [52] L. Qi, H. Cölfen, M. Antonietti, M. Li, J. D. Hopwood, A. J. Ashley, S. Mann, *Chem. Eur. J.* **2001**, *7*, 3526–3532.
- [53] N. I. Kovtyukhova, T. E. Mallouk, *Chem. Eur. J.* **2002**, *8*, 4355–4363.
- [54] B. R. Martin, S. K. St Angelo, T. E. Mallouk, *Adv. Funct. Mater.* **2002**, *12*, 759–765.
- [55] J. L. Wilbur, A. Kumar, E. Kim, G. M. Whitesides, *Adv. Mater.* **1994**, *6*, 600–604.
- [56] A. J. Black, K. E. Paul, J. Aizenberg, G. M. Whitesides, *J. Am. Chem. Soc.* **1999**, *121*, 8356–8365.
- [57] J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature* **1998**, *394*, 868–871.
- [58] R. D. Piner, J. Zhu, F. Xu, S. H. Hong, C. A. Mirkin, *Science* **1999**, *283*, 661–663.
- [59] K. B. Lee, S. J. Park, C. A. Mirkin, J. C. Smith, M. Mrksich, *Science* **2002**, *295*, 1702–1705.
- [60] H.-W. Li, V. O. Beinn, G. Fichet, W. T. S. Huck, *Langmuir* **2003**, *19*, 1963–1965.
- [61] S. H. Hong, C. A. Mirkin, *Science* **2000**, *288*, 1808–1811.
- [62] A. J. Bard, *Integrated Chemical Systems*, Wiley, New York, **1995**.
- [63] C. V. Nguyen, K. R. Carter, C. J. Hawker, J. L. Hedrick, R. L. Jaffe, R. D. Miller, J. F. Remenar, H. W. Rhee, P. M. Rice, M. F. Toney, M. Trollsas, D. Y. Yoon, *Chem. Mater.* **1999**, *11*, 3080–3085.
- [64] K. Yu, B. Smarsly, C. J. Brinker, *Adv. Funct. Mater.* **2003**, *13*, 47–52.
- [65] R. W. J. Scott, S. M. Yang, G. Chabanis, N. Coombs, D. E. Williams, G. A. Ozin, *Adv. Mater.* **2001**, *13*, 1468–1472.
- [66] M. Mamak, N. Coombs, G. Ozin, *J. Am. Chem. Soc.* **2000**, *122*, 8932–8939.
- [67] M. Mamak, G. Metraux, S. Petrov, N. Coombs, M. Green, G. Ozin, *J. Am. Chem. Soc.* **2000**, *122*, 5161–5175.
- [68] B. Oregan, M. Gratzel, *Nature* **1991**, *353*, 737–740.
- [69] I. Soten, Ph.D. Thesis, University of Toronto, **2001**.
- [70] S.-H. Yu, M. Antonietti, H. Cölfen, M. Giersig, *Angew. Chem.* **2002**, *114*, 2462–2466; *Angew. Chem. Int. Ed.* **2002**, *41*, 2356–2360.
- [71] J. H. Schattka, D. G. Shchukin, J.-g. Jia, M. Antonietti, R. Caruso, *Chem. Mater.* **2002**, *14*, 5103–5108.
- [72] D. G. Shchukin, J. H. Schattka, M. Antonietti, R. Caruso, *J. Phys. Chem. B* **2003**, *107*, 952–957.
- [73] L. Spanhel, H. Weller, A. Henglein, *J. Am. Chem. Soc.* **1987**, *109*, 6632–6635.
- [74] F. Campus, P. Bonhote, M. Gratzel, S. Heinen, L. Walder, *Sol. Energy Mater. Sol. Cells* **1999**, *56*, 281–297.
- [75] P. Bonhote, E. Gogniat, F. Campus, L. Walder, M. Gratzel, *Displays* **1999**, *20*, 137–144.
- [76] H.-P. Hentze, M. Antonietti, *Rev. Mol. Biotechnol.* **2002**, *90*, 27–53.
- [77] E. C. Peters, F. Svec, J. M. J. Frechet, *Adv. Mater.* **1999**, *11*, 1169–1181.
- [78] S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, F. Schüth, *Science* **1996**, *273*, 769.
- [79] O. Dag, G. A. Ozin, H. Yang, C. Reber, G. Bussiere, *Adv. Mater.* **1999**, *11*, 474–480.
- [80] Y. Cohen, B. Hatton, H. Miguez, N. Coombs, S. Fournier-Bidoz, J. K. Grey, R. Beaulac, C. Reber, G. Ozin, *Adv. Mater.* **2003**, *15*, 572–576.
- [81] A. G. Cullis, L. T. Canham, *Nature* **1991**, *353*, 335–338.
- [82] V. Hornebecq, M. Antonietti, T. Cardinal, M. Treguer-Delapierre, *Chem. Mater.* **2003**, *15*, 1993–1999.
- [83] A. G. Evans, Z. Suo, R. Z. Wang, I. A. Aksay, M. Y. He, J. W. Hutchinson, *J. Mater. Res.* **2001**, *16*, 2475–2484.
- [84] E. P. Giannelis, *Adv. Mater.* **1996**, *8*, 29.
- [85] S.-H. Yu, M. Antonietti, H. Cölfen, J. Hartmann, *Nano Lett.* **2003**, *3*, 379–382.
- [86] S. Mann, *Angew. Chem.* **2000**, *112*, 3532–3548; *Angew. Chem. Int. Ed.* **2000**, *39*, 3393–3406.
- [87] A. Mamedov, D. M. Guldi, M. Prato, N. A. Kotov, *Abstr. Pap. Am. Chem. Soc.* **2002**, *223*, 173-COLL.
- [88] Y. J. Liu, X. L. Chen, *Mech. Mater.* **2003**, *35*, 69–81.
- [89] M. Antonietti, M. Breulmann, C. Göltner, H. Cölfen, K. K. W. Wong, D. Walsh, S. Mann, *Chem. Eur. J.* **1998**, *4*, 2493–2500.
- [90] T. Asefa, M. J. MacLachan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867–871.
- [91] H. Yang, N. Coombs, G. A. Ozin, *Adv. Mater.* **1997**, *9*, 811.
- [92] P. D. Yang, T. Deng, D. Y. Zhao, P. Y. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244–2246.
- [93] S. M. Yang, N. Coombs, G. A. Ozin, *Adv. Mater.* **2000**, *12*, 1940–1944.
- [94] G. A. Ozin, S. M. Yang, *Adv. Funct. Mater.* **2001**, *11*, 95–104.
- [95] S. M. Yang, G. A. Ozin, *Chem. Commun.* **2000**, 2507–2508.