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# Order−Disorder in Self-Assembled Mesostructured Silica Films: A Concepts Review

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Organization of nanomaterials through self-assembly is an important example of disorder to order evolution of nanoscaled systems. Mesoporous materials show an ordered porous structure at the mesoscale (2−50 nm) whose formation is driven by the fast solvent evaporation during processing. An ordered porous topology is achieved in mesoporous thin films by a combination of sol−gel and supramolecular chemistry using a micelle templated self-assembly process. In the last years an increasing number of scientific articles and reviews have been dedicated to the subject because of its interest for basic science and the envisaged applications in several fields. These materials are obtained through a process which needs controlling of several synthesis and processing parameters; they represent an interesting challenge to our capabilities of understanding order−disorder transitions in complex systems. Order in mesoporous silica films is, in fact, connected to the structural organization of pores, to transitions between different types of phases, the presence of well-defined building block units, and structure in the pore walls. We have critically reviewed the concepts behind self-organization in mesoporous silica films by discussing several aspects in which order is involved.

## Introduction

Mastering order at a nanoscale through self-assembly is one of the most fascinating opportunities of nanoscience. Complex systems show in the range of a few nanometers a surprising tendency to evolve into ordered structures of highly sophisticated architectures. Mesostructured materials are an interesting example of nanoscale systems, whose ability to self-assemble and self-organize is an intriguing challenge to our ability of controlling and understanding disorder to order transitions. Self-assembly is a general phenomenon which is well-known and used in nanoscience to produce ordered structures using well-defined nano-objects. In particular, colloids self-organize into ordered layers during evaporation of the solvent; this is a general phenomenon that is commonly indicated as evaporation induced self-assembly (EISA). EISA has been used to organize nanoparticles in solution that are drawn to the meniscus by convective transport; the capillary forces push organization into close-packed structures.[1,2] An aligned film of carbon nanotubes can be formed simply by evaporation on a hydrophilic substrate of a water droplet containing dispersed carbon nanotubes.[3] These phenomena of organization through evaporation give very ordered structures from well-defined nanounits, such as nanoparticles,[4] nanorods,[5] and nanotubes,[3] and can be used to obtain photonic crystals and several types of advanced materials that need order at a nanoscale to exploit new or exotic properties. Basically these types of phenomena are relatively simple and capillary forces during evaporation drive self-assembly, while in closed systems entropy is often the cause of nano-organization.[6] If we increase the level of complexity using not only nano-objects to achieve self-assembly and somehow we try to mimic natural self-organization to complex architectures, the things become more complicated and the process appears governed by the delicate balance of many parameters and different driving forces. A nice example is represented by mesostructured materials that are obtained through self-assembly of supramolecular templates.[7] The evaporation of the solvent drives the formation and organization of micelles, while polycondensation reaction of building blocks (inorganic or hybrid oligomeric species) at the micelle surface forms the mesostructure backbone. The process is clearly more complex than the evaporation of colloidal solutions because several parameters are involved and the chemical−physical features appear difficult to study. Organization achieved via micelle templates enlarges the possibility of obtaining different types of well-defined and ordered structures. In particular, controlling self-organization through EISA in thin films is even more difficult because the solvent evaporation is very fast and the kinetics of the processes that are simultaneously involved are critical.

Our understanding of order in small scale is heavily challenged by the different possibilities offered by self-assembly of mesostructured materials; order appears when micelles form, but also the building blocks of the inorganic network show small scale ordered structures.

In the present article we will not enter in the details of self-assembly mechanisms, and we will not describe the different systems that have been synthesized; several extensive and detailed reviews are available on the subject.[7,8] A full understanding of the self-assembly process requires crossing information from the existing reviews with the present one. We have used schemes and transmission electron microscopy images to illustrate the different points, and readers should refer to the cited articles in the text for structural data from X-ray diffraction and small-angle X-ray scattering.

This review is dedicated to exploring the concepts behind order and disorder in mesoporous silica films; we have restricted our overview to silica because it is the most popular and common oxide to be prepared as mesoporous thin films and it has some peculiar properties that make this material really interesting to explore order in small scale materials.

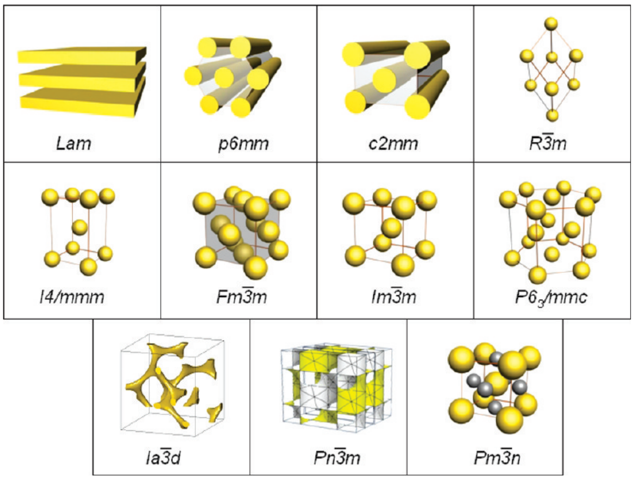

**Figure 1.** 2D (Lam = lamellar, *p6mm*, and *c2mm*), 3D ($R\bar{3}m$, $I4/mmm$, $Fm\bar{3}m$, $Im\bar{3}m$, $P6_3/mmc$, and $Pm\bar{3}n$) and bicontinuous ($Ia\bar{3}d$ and $Pn\bar{3}m$) pore structures obtained in silica mesoporous thin films.

## Types of Order

The first question that we have to pose discussing organization that arises from self-assembly of mesoporous[9] silica films is what type of order we can obtain. Order clearly depends on mutual interactions during processing of several parameters, the kind of "chemical−physical" symphony described by Soler-Illia and Innocenzi;[10] at the moment, however, the scientist-director can only write the music but cannot direct the orchestra. Making an a priori prevision of the porous ordered phase[11] is, in fact, quite difficult, and our ability of producing specific phases basically has relied and still largely relies on a trial and error process. Several types of porous structures have been obtained and described by different groups for silica mesostructured films; we can divide the mesophases in two groups of lower and higher symmetry, that is, two-dimensional (2D) and three-dimensional (3D) phases, respectively. A worm-like disordered phase, with only a local correlation, is also commonly observed as a result of poor ability to self-assemble to an ordered structure; this structure is generally formed when the condensation of the silica backbone is too high or the amount of surfactant too low. Typical 2D structures that have been reported are lamellar[12] and 2D-hexagonal (2D-hex); in general the stability, chemical and mechanical, of the 2D porous phases is much lower than that of the 3D phases, but the possibility of orienting the channels of 2D-hex structures makes them quite appealing for several applications. A typical 2D order is represented by the 2D-hex porous phase with hexagonal plane group *p6mm*,[13,14] another 2D structure that has been produced is the planar rectangular *c2mm* mesophase.[14] Several types of 3D structures have been also reported for mesoporous silica films: the 3D hexagonal (3D-hex) phase, $P6_3/mmc$ space group,[15,16] is one common example. Other cubic structures are formed by different types of cells: a primitive cubic phase, $Pm\bar{3}n$ space group;[8e,17] bicontinuous cubic, $Pn\bar{3}m$;[18] a body centered cubic phase, $Im\bar{3}m$;[19,20] a body-centered tetragonal phase, $I4/mmm$;[21] a face-centered cubic phase, $Fm\bar{3}m$;[22,23] and a double-gyroid cubic phase with space group $Ia\bar{3}d$.[24,25] The different phases are illustrated in Figure 1. How order is finally achieved depends on the ability of the micelle to form and organize in a system where the kinetics of the process is a key parameter. The fast evaporation of the solvent induces the micelle formation, but the nature of the interface, such as micelle curvature, and the interaction at the hybrid interface has also a predominant role.[26] In general, the difficulty to take into account the multiple effects of the many parameters[27] that have been described to affect self-assembly hampers our ability to predict and control the mesophase that will be formed.[28] The process of organization involves the formation of intermediate species, as it has been shown studying the structural evolution taking place during the processing of the silica self-assembled film; the final $Pm\bar{3}n$ cubic structure, for instance, is obtained via the formation of lamellar and hexagonal intermediate structures.[29] The formation of a surfactant concentration gradient, from the air−liquid interface to the film substrate, which is larger in thicker films, is responsible for the presence of the intermediate species,[30] and this the reason why several different phases can be found in the same film. In general, in fact, the chemical−physical phenomena during evaporation are kinetically controlled;[31] a water−surfactant richer liquid−air interface is formed during EISA, and this produces different mesophases in the films. However, not only can several mesophases coexist, but it is even possible to observe one type of mesophase with two well-defined preferential orientations. An example that has been reported is the formation of $Pm\bar{3}n$ phases with (211) and (210) orientations together with the mono-oriented *p6mm* mesophase. The presence of epitaxial relationships between the different phases, such as that one between the $Pm\bar{3}n$ and the *p6mm* phases along the (211) and (01) directions, respectively, favors the presence of different phases.[32]

After film deposition, a mesostructure is finally formed if self-organization has been achieved; the material, however, is not stable, at least until a thermal treatment has

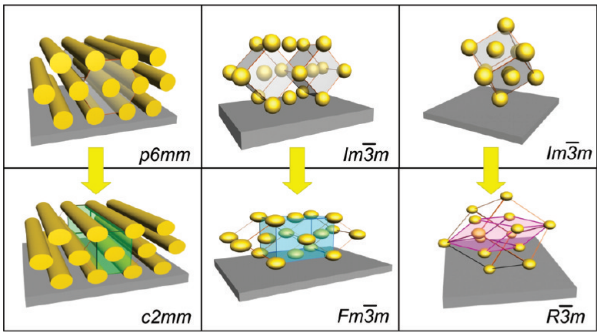

**Figure 2.** Allowed mesophase transitions in ordered mesoporous silica films.

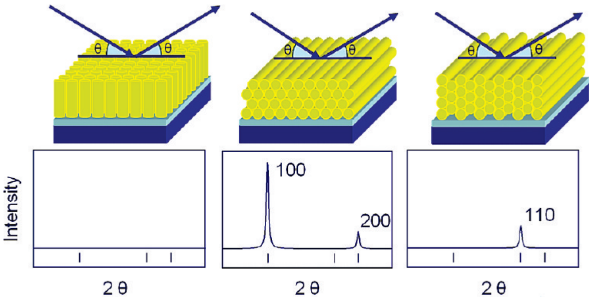

**Figure 3.** Orientations of 2D hexagonal pore structures (above) and corresponding reflection mode X-ray diffraction pattern (below). (Adapted from Figure 4 of ref 42. Copyright 2008, Elsevier).

been done to induce a higher degree of condensation in the silica pore walls. The thermal treatment has, therefore, two effects: condensation and removing of the templating surfactant. The thermal stabilization process produces a shrinkage of the films in the direction normal to the substrate which can have two different effects on the film structure: producing a distortion of the pore shape, generally from spherical to ellipsoidal, and/or inducing a change in the mesophase, that is, in the pore organization. Even if phase transition of the mesostructure is not observed, a strong distortion of the cell parameters can occur upon shrinkage.[33] The phase change has to follow in any case the symmetry rules, and only some transitions are allowed; only few of these transitions have been identified, in particular: from an oriented (10) planar hexagonal *p6mm* to an oriented (10) planar rectangular *c2mm* mesophase;[14] from an oriented (110) body centered cubic $Im\bar{3}m$ to an oriented (010) orthorhombic *Fmmm*,[20] and from an oriented (111) face centered cubic $Fm\bar{3}m$ to an oriented (111) rhombohedral $R\bar{3}m$ phase.[23] Figure 2 shows a scheme of the phase transitions that we have described. A systematic study has been done by Wei and Hillhouse[34] that reproduced the known structures of mesoporous silica films and investigated the change in the mesophase after contraction. One important observation from this work and from a comparison of the data in literature is that not all the known pore topologies can be obtained from the same type of surfactant even if different surfactants can produce the same mesophase. This is an indication that if were able to keep constant all the other variables during EISA processing, the curvature of the micelle and the interactions at the interface have the key role to control ordering. The structure that is obtained at the end of EISA processing[35] is the product of an allowed transition between different porous phases that is thermally induced on the mesophase. The possibility to change the organization in mesoporous films upon external intervention is one of their most striking properties. Until the structure is not finally condensed and rearrangement of the micelles is allowed, the film remains in a kind of tunable state, and the organization can be controlled even in a reversible way.[36] A nice description of this property has been done by Grosso et al. who modulated the film mesostructure by changing the relative humidity in the deposition room; different phase transitions have been described.[37] In this case the water absorption induces a micelle swelling and promotes a change in the micelle organization, if the silica backbone is still enough compliant to allow these transitions. On the other hand this "tunable" property allows film patterning by specific lithographic techniques that are based on mesophase change induced when the material is still in its tunable state.[38] An example is the hexagonal-to-tetragonal phase transformation observed in photosensitive silica mesoporous films after UV illumination.[39]

EISA is not the only method to obtain mesostructure oxide films; it is possible somehow to reverse the approach and use a preordered template film instead of trying to obtain order during processing. This method has been proposed by Watkins et al., who have used selective deposition of silica in a block copolymer film dialyzed by supercritical carbon dioxide.[40] Unlike EISA, this strategy allows preorganization of the template by decoupling the metal oxide condensation and the template self-assembly. Mesoporous silica films with well ordered nanochannels oriented parallel to the substrate have been also produced by this method.[41]

## Defects in the Mesostructure Order

**Point Defects and Linear Defects.** We have seen that several types of porous structures can be obtained, and it is also possible to identify a unit cell of specific dimensions which generates a three-dimensional order. In general, the ordered array of pores in the mesostructured films is well described in terms of a "crystalline-like" structure; even if the silica films are not crystalline they give diffraction patterns when irradiated by X-rays (Figure 3). This is due to the periodic voids in the amorphous network or, if the material is not calcined, to the periodic contrast in the electronic density in correspondence of the surfactant periodic array.[42] The dimensions of the unit cells will be, however, quite larger in comparison with ordinary crystalline materials; instead of a lattice of atoms (0.1−0.2 nm), we have an ordered structure of voids and walls (both in the 2−6 nm range), and consequently the lattice parameters will be on the order of 4−12 nm, which is much higher than the typical dimension of a crystalline structure (~0.5 nm). If we treat mesoporous ordered materials like crystals, we should be well aware that we have to face the presence of several types of defects at different length scales, exactly such as the case of ordinary crystals. At the same time we have to realize that obtaining defects free and monocrystalline-like self-assembled mesostructured films is the ambitious challenge to master a process mainly driven by kinetics.

We can analyze the defects starting from point defects, which in crystalline materials are intrinsic defects that must be present on a thermodynamic basis, such as atomic vacancies. In mesostructured materials, however, vacancies in the ordered array of pores are not thermodynamic defects and are less common to be observed. However, the defects generated by the coalescence of adjacent micelles, which are often observed in mesoporous materials, can be properly considered point defects. This type of defect is generated during the film formation, when the polycondensation reactions are not yet completed. A direct probe of defects has been realized by applying single molecule microscopy to hexagonal mesoporous silica films; closing of pores and small openings in the silica walls between neighboring channels have been observed.[43]

Beside these point defects, which can be considered peculiar of mesostructured films, line defects such as dislocations that are typical of crystalline materials have been also described. Even if the term dislocation has been used to describe linear defects in mesostructured materials,[44,49] these defects cannot move under mechanical stress such as the case for the dislocations in crystalline materials and are only defects in the structural arrangements of pores. The first clear observation of "dislocation" defects in the pore array has been reported by Feng et al.,[44] for mesoporous silica powders with hexagonal mesophase (*p*6*mm*). Two types of dislocations were described, longitudinal edge dislocations and mixed dipole dislocations; the nature of the dislocations, which is similar to those observed in liquid crystals, suggested that they formed in the liquid-crystal-like stage before formation of the silica backbone through polycondensation.[45,46]

This hypothesis has been confirmed by other studies on defects in cubic mesoporous films that revealed the presence of bending deformation, which are also typical of liquid crystals.[47,48] A specific study of linear defects in silica mesostructured films, which have been synthesized by cohydrolysis of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES), has been reported by Brinker et al.;[49] the origin of this type of defects seems correlated with the presence of strain in mesostructured films (Figure 4). The formation of a residual strain in sol−gel films is also a process that involves several processing parameters;[50] in general, the uniaxial shrinkage of the film in the direction normal to the substrate, which arises because the film is constrained to the substrate, produces a tensile stress in the films and a compressive stress in the substrate. In mesoporous films the presence of the surfactant does not avoid the formation of strained films at the end of the process, and residual stress is generally present, such as in the more general case of sol−gel coatings.

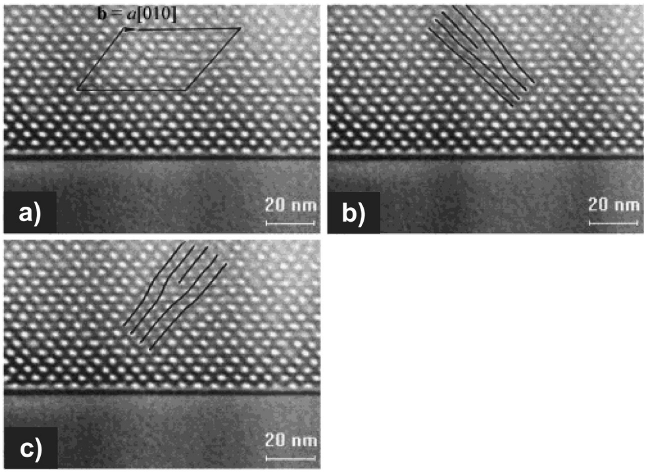

**Figure 4.** Bright-field TEM images showing some examples of linear defects. (Reprinted with permission from Figure 1 of ref 49. Copyright 2003, The American Chemical Society).

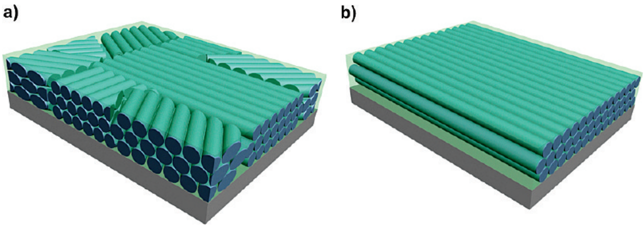

**Figure 5.** 2D hexagonal ordered porous structure with "*polycrystalline*" (a) and "*crystal-like*" domains (b).

**Grain Boundaries, Polycrystals−Monocrystals.** If we describe the mesoporous silica films in terms of crystalline-like materials, the similarity is not restricted to point and unidimensional defects, but we can also observe defects that are typical of polycrystalline materials which are formed of different grains. TEM and small-angle X-ray scattering (SAXS) analysis on mesostructured silica films have revealed that there is a polydistribution of ordered porous domains, "*polycrystalline-like*", which are well oriented along the substrate, but all possible in-plane orientations are also present (Figure 5). Detailed TEM analyses have shown the presence of grain boundaries of different angles at the mesoscale.[14] Quantitative analysis of defects and grain boundaries in mesostructured films of cubic structure ($Im\overline{3}m$) have revealed that low angle, high angle, and translational antiphase domain boundaries are formed in the films.[51,52] The domains are extended in a range of several hundreds of nanometers and exhibit edge dislocations at the boundaries and within the ordered domains. Bend deformations similar to those of nematic liquid crystals have been reported in accordance with the work of Brinker et al.[49] On the other hand, the presence of domains and therefore grain boundaries is even more complex for mesoporous films because domains of different mesostructures can coexist (vide supra): in the same film it is possible to have disordered domains or lamellar structures together with cubic or

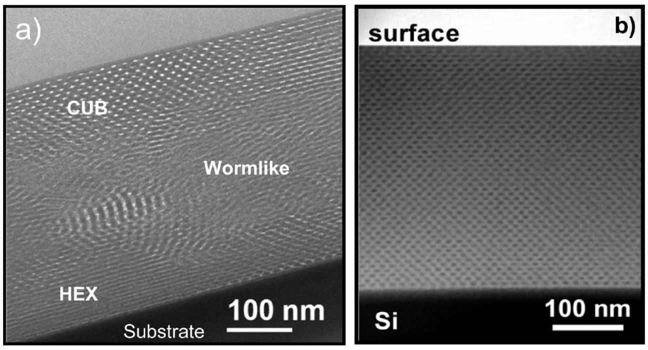

Figure 6. (a) HRTEM image of a mesoporous silica film showing the coexistence of hexagonal (HEX), wormlike, and cubic (CUB) pore domains. (b) HRTEM image of a hybrid mesoporous MTES-TEOS silica film with highly ordered tetragonal pore structure. (Reprinted with permission from Figure 6b of ref 21. Copyright 2005, The American Chemical Society).

hexagonal mesophases.[53] Even if this case represents somehow an extreme, it is clear that the interfaces (solid−liquid and liquid−air) favor this type of multimesostructures; an example is in Figure 6 that shows a high resolution TEM image of a mesoporous silica film section. The film shows the coexistence of different types of ordered domains, hexagonal (at the silicon−film interface), wormlike in the middle, and cubic at the film−air interface. The preparation of a "*monocrystal*", in which the order is extended on the whole film or at least on a longer scale (millimeters to centimeters) by a simple and reproducible route remains one of the main challenges for the exploitation of mesoporous silica films in industrial applications. Clearly if we are not able to master the pore order on a bigger scale we lose some of the main advantages of the material properties. Basically we can think about two different strategies to extend the scale order; one is trying to manage the film formation process by prepatterning the surface that allows a controlled epitaxial growth, while another one is based on the chemical−physical process control during film formation. Two examples of these different strategies have been shown by Kuroda[54] et al. who obtained highly ordered mesoporous films whose organization is extended for several centimeters and Falcaro et al.[21,55] who have fabricated defect-free hybrid silica films even if in a shorter range. The two examples are important to withdraw some basic information about mesoporous film formation, because if clearly the epitaxial controlled growth allows alignment of pores on a rubbed surface, adjusting the kinetics of EISA parameters allows also moving a step ahead on the route of self-assembly.

## Order Disorder in the Pore Walls

The dimension of the pore walls is an important parameter to take into account to control the mechanical properties[56] and the durability of mesoporous films.[57] In general, increasing the pore wall thickness is seen as the simplest route to enhance the overall performance of the material; especially in the case of silica films it is important not to focus only on the dimensions but also on the structure of the silica network that forms the backbone of the mesoporous film. One of the critical issues in the field of mesoporous self-assembled films remains our inability to obtain crystalline silica films with an organized porosity. While this target has been somehow achieved in the synthesis of hybrid silica powders, it still remains a kind of "holey grail" for films. This is also a clear indication that the different conditions of preparation between monoliths and films change the chemical−physical conditions during material processing. On the other hand, crystalline walls are easily obtained in films based on transition metal oxides, and several examples, such as perovskite mesostructured films, are reported in the literature.[58] The pore walls are generally formed by crystals of dimensions up to few nanometers, and crystal growth is achieved by a controlled thermal treatment. The case of mesoporous silica crystallization of the walls has not yet been reported, but because of the poor hydrolytic stability of silica the achievement of this goal could really boost applications for mesoporous films. The beautiful organized layered structures in the pore walls found by Inagaki et al. for hybrid silica materials have not yet been reproduced in films.[59,60] Even if real silica "crystalline" walls have not been synthesized in mesoporous films, several noticeable works have been dedicated to achieve a control of the material property by managing the silica structure at a very fine level. The dimension of the silica pore wall is still relevant to affect the materials properties; in particular we can distinguish three different length scales: an atomic scale, over 1.5 − 2.5 Å, a molecular one, from 2.5 to 4.5 Å, and finally the "network" scale, within a few nanometers. The molecular scale is particularly interesting because it is associated with medium-range order; at this scale we have the cross-linking of the glass network with the occurrence of clusters and rings. Medium range order can be observed at the molecular scale with the formation of rings of different dimensions, which range from 2-fold up to 6-fold rings. The role of these basic units in the silica network of the films is not trivial, in the sense that several of the material properties are affected by their presence. It is noticeable that the dimensions of the silica pore walls are in the mesoscopic range, which is exactly the scale for silica glasses that would develop some local order through the formation of organized domains.[61] In silica glasses, the size of the "domains", which are likely to be amorphous, is typically $< 10$ nm and can be estimated from the frequency of the "Boson" peak observed in the 3−50 $\text{cm}^{-1}$ Raman frequency range.[62] The presence of cyclic species in silica precursor solutions has been well described by $^{29}$Si nuclear magnetic resonance (NMR) experiments;[63,64] the particular processing conditions that are used for self-assembly of silica films (the low pH) can produce the formation of middle range ordered units, such as fourfold and threefold rings. To assess the presence of these structures in thin films is, however, not a simple task because the only techniques that can give a direct in situ indication of the presence of silica rings are FTIR and Raman,[65] which are quite difficult to perform on thin films (Raman) or can give only limited information (FTIR). The spectra of as-deposited mesoporous silica films have shown that some of these cyclic species are retained in the structure after deposition even if at temperatures higher than 350 °C they generally disappear. Cyclic species, especially those of lower dimensions such as twofold, threefold, and fourfold rings are, in fact, thermodynamically unstable, and during thermal treatment the medium range order is easily lost. In particular, the presence of specific vibrational bands associated with disorder−order transitions in the silica structure have been reported upon FTIR analysis of silica mesoporous thin films.[66] These disorder-induced optical modes are due to the large interface in mesoporous silica films and correlated to bond strains. In the case of mesostructured porous films, the pores are ordered, and the pore walls are amorphous; however, a medium range order (the silica rings) is present in their structure. This is not just an "academic" classification because it has been demonstrated that the presence of silica rings in the pore walls strongly influences the mechanical properties, such as the elastic modulus. A very nice demonstration of how much the presence of medium range order can affect the properties of the films has been reported by Brinker at al.[67] It is really interesting to notice that the reduced dimensions of the silica walls (typically in the range of 2−3 nm) somehow force the formation of a large population of four-member rings and a decreased population of larger rings. The reduced dimensions push the medium range order with respect to amorphous bulk silica and xerogel materials. The formation of small silica rings is also the product of the dehydroxylation[68] of the silica surface, and the thermal history of the sample is very much affecting their concentration. The presence of these medium range order species is also quite well assessed for silica mesoporous powders[69] and can be taken as a peculiar characteristic of silica networks in small dimensions. Getting the control of medium range structures, such as silica rings, within the silica network in mesoporous films is, however, a difficult task. Mastering the material properties through the structure at this scale is limited by the difficult detection of silica rings into the mesoporous film network. On the other hand silica cyclic species are already present in the precursor solution; their nature and amount are strongly dependent on aging which is an important parameter to take into account to design the right mesophase.[70] The silica sol is formed of small oligomeric rings and cage-like species that with aging time are linked to form larger silica clusters. An example of silica cyclic species that can be found in silica mesoporous walls is shown in Figure 7.[71] A good experimental evidence of the effect of aging has been reported by Hillhouse and co-workers: silica condensation and cluster growth in the precursor sol have been found to be unambiguously correlated with the formation of different mesophases in the film; aging of the silica sol decreases the interfacial curvature and gives a different order topology.[72] Figure 8 from ref 72 shows the effect of aging as a function of Si:EO (EO = ethyleneoxide) ratio in silica mesostructured films; if the ratio is fixed, different mesophases are produced in the film by changing the aging time.

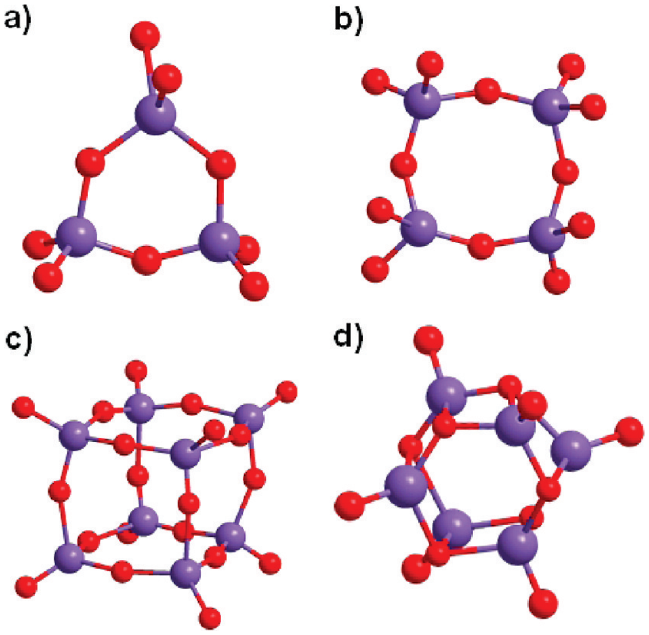

**Figure 7.** Examples of silica cyclic species in mesoporous silica walls.

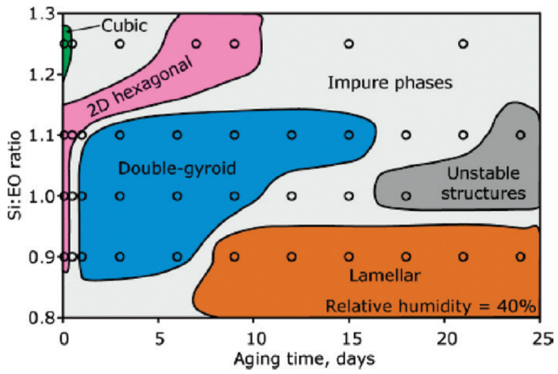

**Figure 8.** Influence of the processing parameters on self-assembled silica films obtained via EISA. Effect of the [Si]/[EO] ratio and aging time on the structure of the resulting ordered mesoporous structure at relative humidity of 40%. (Reprinted with permission from Figure 5 of ref 71. Copyright 2007, The American Chemical Society).

It is also possible to design the silica network structure using predefined framework units, and an elegant approach has been proposed by Kuroda and co-workers who synthesized specific building blocks.[73] Siloxane cages are a nice example of symmetrical units that can be used as molecular building blocks for silica and hybrid networks; the molecular design of these building blocks with alkoxy functionality allows formation of a siloxane network with well-defined silica units.[74] A drawn example of the possible structural building blocks, cyclic species, and cages that can form the silica backbone is shown in Figure 9. This represents an extension of the concept of order in the silica mesoporous film framework where "bricks" of specific geometry are used to build up the network.[75] The pore walls are still amorphous, but some order is given by the presence of cage-like units; enhanced properties could be expected for this type of

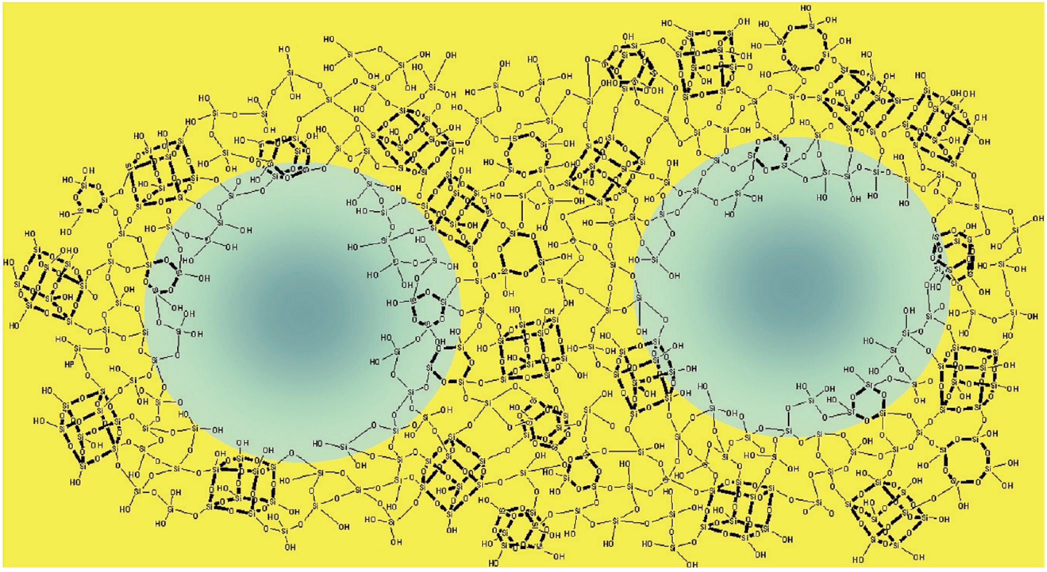

**Figure 9.** Picture of mesopore walls made with silica cyclic species embedded.

silica mesoporous films built by molecularly designed building units even if experimental support still has to be clearly shown.

## Order and Properties

One of the main questions which is addressed to researchers working on mesostructured porous films concerns the advantage of the pore order and how the order affects the film properties. These are clearly critical issues and deserve strong experimental evidence to reply in a proper way; in general, in fact, the supporting experiments require a high level of sophistication. The clear advantage of getting ordered porous structures has been shown by Brinker et al., who measured the elastic modulus of thin mesoporous silica films.[67] They have found a modulus–density scaling relationship for cubic (C), hexagonal (H), and worm-like disordered (D) mesoporous silica prepared by surfactant directed self-assembly. Mesostructured porous silica films have shown a hierarchy of modulus values, $D < H < C$, which depends on the specific pore topology; order versus disorder changes the mechanical properties;[76] the higher the symmetry, the higher the elastic modulus of the material.

The advantage of getting an ordered porous structure is, however, not only linked with changes of some general properties of the material; the possibility of obtaining ordered pores is, in fact, intuitively correlated to diffusive processes, and interconnected and ordered paths represent an intrinsic advantage for effective mass transport. Several works have been devoted to assess how the topology of the ordered porosity affects the diffusion within the films,[77,78] and the order has been found to be the most important factor to take into account for efficient design of a high diffusivity material. The experimental data from different researchers indicate that there is a general correlation between diffusion and topological order of the pores; the diffusivity decreases following this order: gyroid bicontinuous → orthorhombic and cubic → 3D-hex → 2D-hex and rhombohedral.[79] Diffusion in 2D-hex structures has clearly shown a strong dependence on the orientation of the channels with respect to the film substrate; films with cylindrical mesopores oriented parallel to the substrate[80] have been found to block the sensing element.[81] In this case the effect of disorder–order in the mesostructure has been specifically evaluated by electrochemical impedance spectroscopy experiments. Accessibility in 2D rectangular *c2mm* films (which are finally obtained upon shrinkage of *p6mm* 2D-hex films) with a full alignment of the channels parallel to the substrate has been compared with respect to *c2mm* films with only oriented domains.[34] The disordered *c2mm* films have shown a higher accessibility than well organized *c2mm* silica mesoporous films. In the evaluation of these results it should also be considered that not only order but also accessibility and the presence of microporosity, which is generally present in films synthesized from block copolymers,[82] have an important role. Beside electrochemical evaluation of diffusion, some sophisticated experiments have also been performed by single molecule fluorescence microscopy[83−85,43] and positronium time-of-flight spectroscopy to test the accessibility of mesoporous films.[86] In particular, the experiment of Mills et al. has been realized on 2D-hex and cubic mesoporous silica films;[86] also in this case the experiments performed on 2D-hex films have revealed that the diffusion coefficient is an order of magnitude higher in the system with the mesochannels aligned to beam direction.

## Controlling the Order: Orientation of the Pores

We have seen that different types of porous structures can be obtained in mesoporous silica films, and it is possible to design, within some limits, the material properties that are connected to the porous topology. Mesoporous films showing a 2D phase organization, such as the 2D rectangular *c2mm* and the 2D-hex *p6mm*, have a lower symmetry with respect to 3D structures, but the

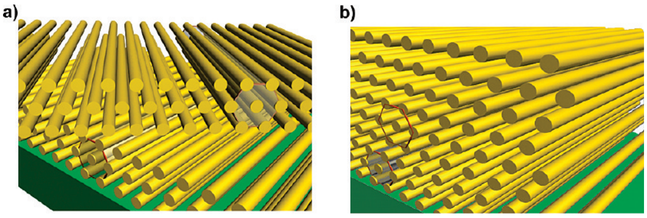

**Figure 10.** Different possible orientations of 2D hexagonal stacks of mesopores in a self-assembled silica film: random (a) and full (b) uniaxial in-plane orientation.

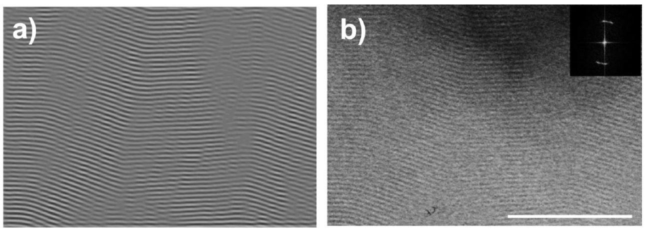

**Figure 11.** (a) Top view TEM image of silica film having zigzag mesoporous structures with fixed kink angles. (b) Reconstructed image of (a) from the fast Fourier transform image, scale bar: 100 nm. Inset: fast Fourier transform image. (Adapted from Figure 6a,b of ref 99. Copyright 2008, The American Chemical Society).

possibility of controlling the mesophase alignment, as we have seen, makes them very attractive. The question is, therefore, how to obtain a preferential orientation of the channels; many researchers have applied plenty of strategies to achieve this goal. Just some examples of the different opportunities to obtain oriented mesochannels in silica films through the highly flexible bottom up EISA route are electrochemical driven self-assembly,[87] dip coating under a steady-homogeneous high magnetic field parallel to a substrat,e[88] and photo-orientation on a photo-cross-linkable polymer film.[89]

We can align the mesochannels along the orthogonal and parallel directions with respect to the substrate, and the strategy to control orientation of 2D mesophases depends on the direction of the channels. In general, to achieve a macroscopic orientation with in-plane alignment is easier, and several syntheses based on epitaxial growth have been reported.[90,91] A true fully ordered mesostructure is, however, obtained only if the channels show the same in-plane uniaxial orientation in a large length scale (Figura 10) and are not only generally aligned in directions parallel with respect to the substrate. The group of Kuroda has done a systematic work on the subject, and they have successfully obtained oriented silica mesochannels in 2D hex structures using polyimide Langmuir−Blodgett films[92] or rubbing treated polyimide films[93,94] to coat the substrate. Clearly the surface properties govern the alignment process, and the channels orientation appears strongly influenced by the interactions between the substrate surface and surfactant molecules.[95] Alignment of mesochannels of different extents has been reported for mesoporous silica films deposited on mica[96] and oriented silicon wafers (110).[97] In this case the substrate itself, without any modification, is able to orient the mesophase; an example is the full in-plane and out-of-plane alignment of hexagonal cylinders that has been observed on freshly cleaved mica substrates.[96] The methods of orientation that do not require a pretreatment of the substrate are clearly more feasible for applications; a more generic method is the application of a hot jet air flow[98] to a droplet of precursor solution after deposition on the substrate. In this case because the mesochannels will be oriented along the direction of the air flow, orientation of multilayered mesostructured films can be achieved; different layers can be oriented in different directions independently of the type and even shape of the substrate. Uniaxial alignment of the channels is not, however, the only possible form of in-plane orientation;[99] steric hindrance effects between the hydrophilic head of adsorbed surfactant molecules and silica oligomers on an aligned rubbing-treated polyimide film give two distinct alignment directions with a zigzag porous structure and a fixed kinky angle. (Figure 11)

Obtaining ordered arrays of channels that are orthogonally oriented with respect to the substrate is more difficult but some successful examples have been reported so far; one possible route is self-assembly in a confined environment with 1D orientation and controlled growth on a prepatterned substrate. Porous alumina membranes, which have ordered and vertical monodimensional (1D) channel structures, have been used as the templating environment for mesoporous silica.[100,101] TEM and X-ray diffraction (XRD) have shown that the pores within the membrane are oriented in a parallel direction with respect to the alumina channels.[102] This route is, however, not suitable for films, and other specific methods based on electrochemically assisted self-assembly[87] and nanometer-scale epitaxial growth[103] have been developed. Both the methods allow achieving vertical alignment of oriented hexagonal channels even if they have some limitations given by the need of a specific substrate. The control of pore orientation in 2D-hex structures is, however, not restricted to the choice of orthogonal−parallel directions with respect to the substrate; it is also possible to produce tilted mesochannels by modifying the substrate with PEO−PPO copolymers to obtain a chemical neutral surface that promotes the alignment.[104]

We have seen that the role of the interfaces in the alignment process is crucial, and most of the successful examples are due to controlled epitaxial growth of the films; it has to be underlined, however, that the orientation is controlled by both interfaces, air−film and film−substrate, and homogeneous layers can be obtained only balancing the interfacial energies.[105] It is otherwise quite common to observe different structures or different levels of organization at the two interfaces and in the middle of the film,[106] which is a clear indication that not only the solid−liquid interface plays a major role to direct organization during EISA.

## Future Outlook

Controlling order−disorder transitions and mastering self-organization into ordered structures at nanoscale is still an open task. Self-assembly of mesoporous ordered silica films is an example of such complexity, that understanding and controlling the different levels of order that are involved in the process are a stimulating challenge. Order evolves from self-organization of templating micelles, but the large number of parameters to be controlled and the lack of systematic basic data still limit our ability to produce well controlled and oriented pores with specific topologies. Several issues have to be settled to reach a full exploitation of the potentialities of the material; in particular, the weak chemical durability under hydrolytic conditions is a major drawback for silica mesoporous films, and a future goal should be obtaining ordered pore walls, at least as hybrid silica. A natural evolution is in the direction of even more complex materials through self-assembly, which means hierarchical porous materials;[107] the different orders of porosity should show both organized structures possibly obtained through self-assembly. Controlling order means also designing the properties as a function of applications and enlarging our perspective on the different complex interactions in the nanoworld.

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(9) The term mesoporous is used, in general, to indicate porous materials whose pore dimension is in the meso-scale, 2−50 nm, following the IUPAC nomenclature. This definition is quite wide and does not specify if the pores are organized. Even if within the scientific community the definition of mesopores has a general meaning and is widely used to indicate both mesostructured and mesoporous organized materials, we should be aware that we are dealing with quite different objects. Mesostructured materials indicate that the micelles form an organized array within the framework, while ordered mesoporous materials are obtained only after the removal of the organic template. Periodically organized mesoporous thin films (POMTFs) is another definition that is currently adopted in the literature, even if it should be specified that the material is obtained trough a self-assembly process with a template.

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