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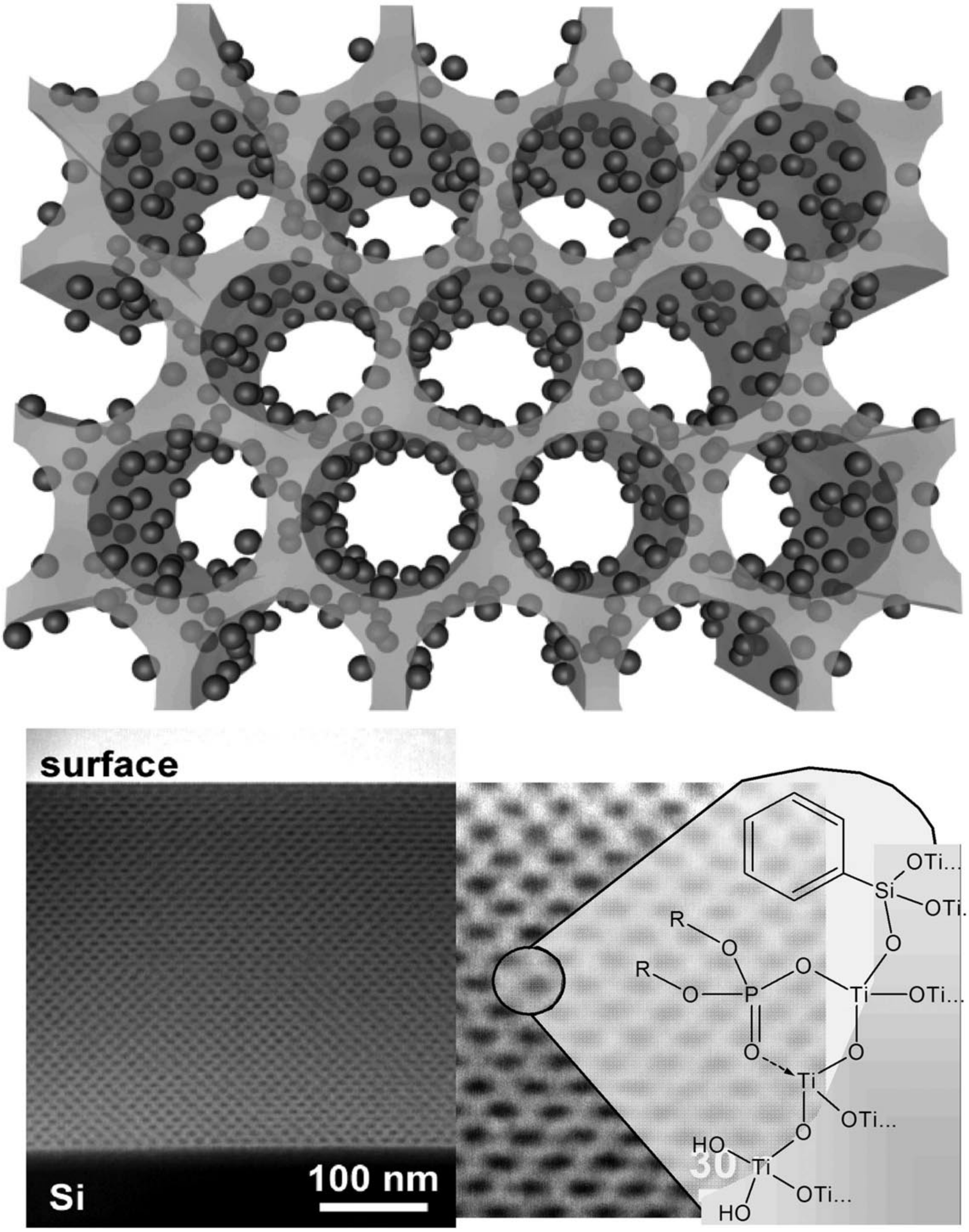
Hybrid Mesoporous Films

An Organised Functional Nanofacility



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Mesoporous Hybrid Thin Films: The Physics and Chemistry Beneath

G. J. A. A. Soler-Illia*[a] and P. Innocenzi[b]

Abstract: Mesoporous films containing organic or biological functions within an organised array of cavities are produced by combining sol–gel, self-assembly of supramolecular templates and surface chemistry. This paper reviews the essential physics and chemical concepts behind the synthesis of these complex multifunctional materials.

Keywords: mesoporous materials • organic–inorganic hybrid composites • sol–gel processes • thin films

A Quick Glance at Mesoporous Oxide and Hybrid Materials

Hybrid materials are becoming an increasing subject of study, due to the possibility to combine inorganic, organic, and even biological functions in a tailored matrix or nanocomposite.[1,2] Among these exciting and innovative materials, mesoporous hybrids are a fine example of a multifunctional system in which an inorganic or a hybrid organic–inorganic matrix (or framework) presents tailored pore sizes, the surface of which can be modified by organic or bioactive functions.[3–5] A great number of characteristics, including framework nature (composition, crystalline structure and crystallite size), high surface area, pore dimension, shape, surface, accessibility and pore array symmetry and interconnection can be tailored, and even tuned, in few finely controlled synthesis steps. These materials present an increasing interest and potential in several fields in which a large functional interfacial area contained in a robust framework is required (e.g., for selective columns, exchangers, (bio)catalysts, nanocomposites for energy applications, etc.). The capability of changing the characteristics of the inorganic framework and the pore surface and/or interior in separate ways leads to an amazing potential in tuning optical or electronic properties. Moreover, a void or functionalised pore system is an invitation to use these nanoconfined spaces as nanoreactors (for the construction of embedded nanoparticles or polymers), and thus creating advanced ordered nanocomposites with perfectly calibrated interfaces. With regard to bio-nanotechnology, nanometric to submicrometric pore sizes are interesting for the interaction with proteins, polynucleotides or for the inclusion of a variety of biological nanostructures from enzymatic systems and liposomes to cell membranes to ion channels.

The possibility of processing mesoporous hybrid materials as thin films is especially interesting, for the combined properties of a thoroughly tailored pore system and the inherent features of thin films (i.e., accurate control of thickness, composition, transparency, presence of electrodes, possibility of multilayer stacking etc.).[6] Moreover, a wide variety of inorganic or hybrid frameworks can be easily obtained, as evaporation-based methods are usually more flexible than precipitation and can be thoroughly studied by in-situ techniques. The control of chemical and processing variables permit the easy creation and reproduction of an amazing library of functional-pore arrays in which tailored diffusion of substrates is possible. These functions can be in turn activated or modified by solicitations such as light, current or a changing environment, making mesoporous hybrid thin films (MHTFs) an exciting prospect for several nanotechnology applications (sensors, actuators, separation and interfacing devices, etc.).[6,7]

The need for mesoporous hybrid thin films (MHTF) has been driven historically by the quest for ultralow *k* dielectrics and low refractive index materials with a good mechanical stability and a hydrophobic nature. Hydrophobic or

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[a] Dr. G. J. A. A. Soler-Illia
Unidad de Actividad Química
Centro Atómico Constituyentes
Comisión Nacional de Energía Atómica
Av. Gral Paz 1499 (B1650 KNA) San Martín
Pcia de Bs.As (Argentina)
Fax: (+5411) 6772-7886
E-mail: gsoler@cnea.gov.ar

[b] Prof. Dr. P. Innocenzi
Dipartimento di Architettura e Pianificazione
Università di Sassari, Nanoworld Institute
Palazzo del Pou Salit, Piazza Duomo 6
07041 Alghero (SS) (Italy)

closed porosity can be used as a means to design new materials with ultralow *k* values, in order to accomplish several very strict requirements to be integrated with the performance specifications by the microelectronics industry. The ability of shaping mesoporous materials as thin films leads to other sought applications, such as sensors, delivery devices or controlled bioceramics. In the first case, 100–500 nm thick films with accessible porosity should allow a rapid transit of analytes, drugs, signal or trigger molecules across nanomembranes. Film-processing procedures permit the stacking of thin films with different characteristics, thus leading to multilayer systems, each layer leading to a peculiar chemical property located in a well-defined position in space. Transparent films containing light-responsive functions can be combined with nonlinear optical chromophores to produce multifunctional photonic devices.[8,9]

This paper presents the chemical concepts that lie beneath the complex phenomena involved in the production of MHTFs, particularly in oxide-derived materials. We will first briefly comment on the synthesis methods and characterisation techniques specifically needed to understand structure, orientation and composition of MHTFs. Understanding these phenomena needs complementary techniques. Second, we will discuss the aspects regarding film formation, stabilisation and template elimination. All three processes are relevant to several central aspects, such as pore orientation, surface or accessibility, which are crucial to the final performance. A thorough understanding and further research in this topic is needed to evolve towards system design versus the trial and error approach. We will finally aim at illustrating the possibilities of MHTFs with several application examples.

Mesoporous Films: An Overview of Synthesis and Characterisation Methods

Typical TEM and SAXS patterns of selected ordered and oriented mesoporous thin films are shown in Figure 1. The dark periodic structure observed in the micrographs is the matrix or framework, which is composed of a metal–oxo network, in the case of mesoporous oxides; as we will see below, this framework can also contain organic functions. The light spots correspond to the pore system; pores can be filled with the template (in a mesostructured material), or void (in a mesoporous material). The pore surface or interior can also be modified by organic moieties, polymers or nanoparticles. The ordered arrangement of the pores leads to periodic contrast differences, producing diffraction patterns that are characteristic of a given mesophase.

The chemical paths towards these materials with complex and perfect organisation at the mesoscale implies essentially, a combination between the *sol–gel chemistry* of the inorganic precursors (alkoxides, organoalkoxides, salts etc.) and the *self-assembly* features of the organic pore templates (typically, surfactants). Knowledge of the chemical concepts related these two fields is required to produce the appropriate "nano building blocks" (NBBs) that will build up the mesostructures, and to control the complex assembly processes between them.

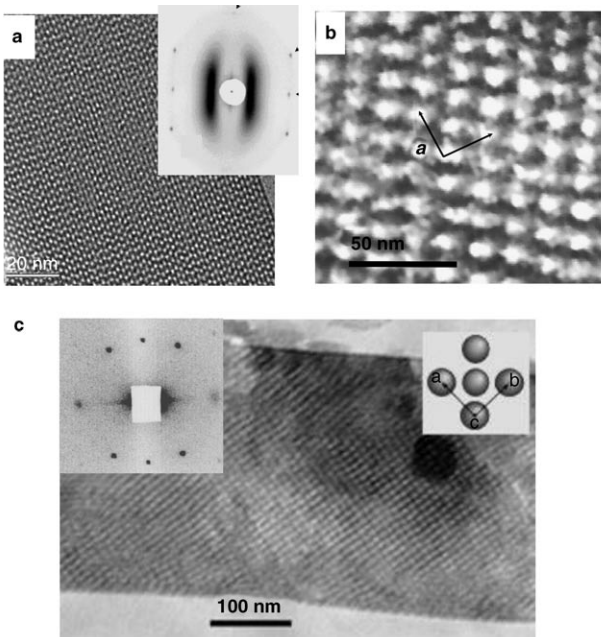


Figure 1. Typical TEM micrographs and 2D SAXS patterns of mesoporous thin films. a) 3D hexagonal silica, templated with CTAB, a cationic molecular surfactant (TEM image: C. Marchi, LNLS, Campinas). b) 3D cubic zirconia, templated with F127, a nonionic polymeric surfactant (TEM image: P. B. Bozzano, UAM, CNEA, Buenos Aires). c) Side view of a cubic titania thin film (adapted from reference [25]).

Sol–gel processing, based on the controlled polymerisation of inorganic molecular precursors in mild temperature conditions, organic solvents, and controlled amounts of water is crucial in the development of synthesis routes of the inorganic NBB. Oxide formation by the sol–gel process implies connecting the metal centres with oxo or hydroxo bridges, therefore generating metal–oxo or metal–hydroxo polymers in solution.[10] Hydrolysis and condensation reactions are akin to activation and propagation steps found in organic polymerisation. Hydrolysis of an alkoxy group attached to a metal centre leads to hydroxyl–metal species [Eq. (1)].

$$\mathrm{M{-}OR + H_2O \rightarrow M{-}OH + ROH} \tag{1}$$

The hydroxylated metal species can react with other metal centres leading to condensation reactions, in which an oligomer is formed by bridging two metal centres. Condensation can lead to an oxo bridge, and water or alcohol is eliminated [Eq. (2)].

$$\begin{gathered}\mathrm{M{-}OH + XO{-}M \rightarrow M{-}O{-}M + X{-}OH}\\ \mathrm{X = H \text{ or } R}\end{gathered} \tag{2}$$

In the case of olation, an addition reaction takes place, and a hydroxo bridge is formed [Eq. (3)].

$$\begin{aligned}&M{-}OH + M{-}OH \rightarrow M{-}(OH){-}M{-}OX\\&X = H \text{ or } R\end{aligned} \tag{3}$$

Chemical control of activation/polymerisation reactions [Eqs. (1)–(3)] permits us to tailor the size, shape and surface (i.e., the presence of polar $-OH$ groups, or hydrophobic residues) of the inorganic polymers or colloids. By tuning their hydrophobic/hydrophilic characteristics, it is also possible to tune the interactions with the organic templates. In silica-based systems, hydrolysis has to be catalysed by submitting to low pH values; condensation is minimised at pH values between 1 and 3. For transition-metal oxide precursors, hydrolysis and condensation are fast processes, and highly acidic media ($pH < 1$ for M^{IV}) are required to avoid extended condensation.

The NBBs that form the material framework can be purely inorganic (i.e., metal–oxo polymers) or hybrid organic–inorganic. In the latter case, the one-pot synthesis of MHTFs implies that organically modified alkoxides (OMA) are used as molecular precursors during sol–gel reactions. The most used Si^{IV}-based OMAs, $R'_{(4-n)}Si(OR)_n$, have one or more organic groups bonded to the central atom, and the covalent nature of the $Si{-}C$ bond assures the hydrolytic stability during sol–gel reactions. The wide variety of the available organically modified alkoxides greatly enlarges the family of MHTFs that can be produced. The OMAs can be also co-reacted with transition-metal alkoxides or metallic salts to give a great variety of hybrid materials. Another group of OMAs has a special role in the synthesis of MHTFs: the bridged silsesquioxanes, because they offer the possibility to synthesise mesostructured materials the organic groups of which are within the pore walls. Using this approach, Inagaki and co-workers[11] were able to obtain hybrid pore walls with "crystalline" nature; this was achieved first in powdered samples and is currently being adapted to thin films. Other functional precursors (typically, $R{-}SiX_3$, or $R{-}GM(OR)_3$, in which G is a grafting function such as a complexing group) can be used in combination with MX_4 precursors, tailoring the compatibility with organic species such as monomers, polymers or surfactants.

The hydrolysis and condensation characteristics (i.e., reaction rates, solubility, connectivity etc.) of the functional precursors are of course different from the simple precursors. However, a vast knowledge base is available from the hybrid materials community, and in principle, one should be able to control synthesis conditions suitable to create oxide, mixed oxide or hybrid networks from any set of precursors, even in mixed oxides in which the cations have markedly different hydrolysis–condensation characteristics.

Self-assembly can be defined as "the ordering of molecules with no external effort". Asymmetric molecules such as surfactants can spontaneously self-assemble in micelles when their concentration in a given solvent is higher than the critical micellar concentration (*cmc*). Micelles are supramolecular NBBs. At higher surfactant concentrations (in the order of 20–70 % mass weight), micelles can in turn assemble in liquid crystalline arrays; some of these arrays possess high ordering at the mesoscopic scale. Ordered liquid-crystal phases are the scaffold for mesoporous materials. Again, an enormous knowledge base is available from the surfactant and polymers community, and the surfactants used in the actual synthesis are just the tip of the iceberg. The mesoporous community could gain also a lot of predictive insight by using the classical polymer approaches (phase diagrams, quantifying interactions, role of the hydrophilic–lipophilic balance (HLB) and excluded volumes, selective functional copolymers etc.).

In summary, to synthesise an organised mesoporous material, the framework NBBs obtained by sol–gel chemistry should be co-assembled with the template NBBs, in an adequate manner, in order to obtain the desired mesophase with the desired framework composition. An important point is that the framework and the template are in contact along the "hybrid interface", which in the case of a mesoporous material represents as much as $1000\,m^2g^{-1}$. An important fraction of the energy towards stabilisation of a mesostructured material arises from favourable interactions between both kinds of NBBs at this hybrid interface. Therefore, the interest in matching these interactions by tuning the hydrophilic character of the framework NBBs to the groups present at the surface of the template NBBs, as suggested by the modulation at the hybrid interface (MHI) mechanism.[4]

One can in principle imagine a retrosynthesis-like rationale such as the one used in organic synthesis, in order to have an overview of the NBBs (i.e., the pieces of the puzzle) needed to design a successful synthesis. In the case depicted in Figure 2, the "nanosynthon target" for a mesostructured material is a micelle, surrounded by adequate inorganic NBBs; this motif, repeated, generates the periodic mesostructure. This nanosynthon can be in turn decomposed into the fundamental NBBs: inorganic oligomers and surfactant molecules. Sol–gel and self-assembly procedures should be able to provide these NBBs. From this simplified view, it is clear that the inorganic oligomers should be hydrophilic in order to provide the proper interactions at the inorganic–organic interface. We can affirm that the first concepts towards design are: 1) to know the nature of your building blocks and 2) to put them in the right place. With these simple principles in mind, a number of systems can be assembled, ranging from any simple mesoporous silica to more complex composite metal/mesoporous silica reported

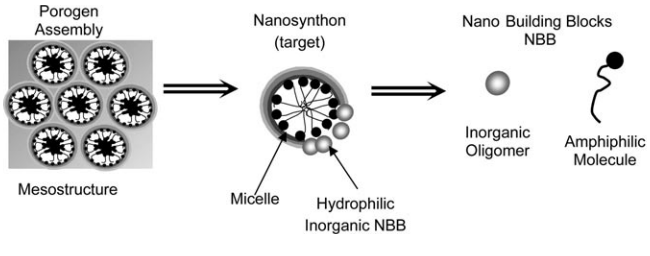


Figure 2. The retrosynthesis path of a mesostructured material.

by Brinker and co-workers.[12] Notwithstanding, the detailed thermodynamic and kinetic aspects of any particular system (i.e., the detailed sol–gel chemistry features, the possible mesophases arising from the interactions between the porogen molecules and the inorganic NBBs, the assembly sequence) must be taken into account, as will be discussed below.

Evaporation-induced self-assembly: Mesoporous films are typically produced after evaporation of solutions containing an inorganic precursor (alkoxide, chloride or mixtures of both), an organic supramolecular template (mostly ionic, nonionic or polymeric surfactants) and some additives (in general, acidic or complexing molecules to control pH, thus avoiding inorganic extended condensation) dissolved in a volatile solvent (mostly alcohols or ethers, such as THF). A number of synthesis procedures have been developed; the concepts behind these procedures are beginning to be understood and will be discussed in a later section. In principle, pore size and symmetry can be adequately tuned by the use of the organic template, from relatively small ionic surfactants to amphiphilic block copolymers.[13] The nature of the wall (whether inorganic or hybrid) and surface can be controlled by choosing the adequate precursor and controlling the sol–gel chemistry of the metal centre.[10] Deposition techniques are varied: from controlled drying of deposited droplets to dip- or spin-coating. The deposition environment, the evaporation process and the resulting film thickness are important not only for the formation of porosity, but also for the symmetry of the pore array. The complex processes taking place during solvent evaporation and subsequent formation of an inorganic-template organised mesophase can be overall ordered in what Brinker and co-workers coined as "evaporation-induced self-assembly" (EISA).[14] At present, there is a sound library of synthesis procedures that permits the creation of mesoporous thin films with a great variety of wall compositions, pore sizes and pore system symmetries.

There are two main routes to incorporate organic functions into mesoporous matrixes; these are shown schematically in Figure 3: 1) "one-pot" synthesis, by co-condensation of a functional inorganic precursor, such as an organosilane, with another precursor in the presence of templates or 2) addition of an organofunction by post-synthesis treatment of a mesostructured or mesoporous material, either by solution impregnation or by exposure to volatile vapours (post-grafting).

It is clear that the availability of large surface areas, rich in silanols or other M–OH groups, provides a simple and immediate route to functionalise the pores, leading to many different types of surface-modified mesostructured hybrid films. In anhydrous conditions, post-grafting can also take place by breaking Si-O-Si bonds, "through a nucleophilic displacement at the silicon atom by the alkylsiloxane group of the silylating agent".[15] Post-functionalisation has been largely exploited (mainly in powders) to graft on the pore surface a variety of functional organic molecules. The one-pot route (i.e., including the organic function in the film formation step) remains, however, a very attractive synthesis, as it constitutes the easiest way to grant incorporation of organic groups embedded within the metal–oxo skeleton. Moreover, the presence of the organic dangling groups seems to play an important role during EISA, and, in certain cases, can direct to one or another mesostructure. Both routes are in fact complementary, and their utilisation depends on the characteristics desired for the mesoporous system. Table 1 summarises the differences between both methods.

Post-functionalisation might seem an easier route because the template can be removed in a previous step, thus clearing the surface sites to selectively attach a new function. It should be stressed that the reactivity of surface silanols is not always easy to control and different species (isolated, terminal, geminal or hydrogen bonded) react in different ways. The control of the extent of grafting reactions is, therefore, an important drawback of post-functionalisation. Moreover, depending on the post-grafting conditions (solvent, function solubility etc.), the framework can be partially dissolved or M–O–M bonds can be cleaved in the procedure. On the other hand, "one-pot" synthesis is somehow complicated by the presence of organically modified alkoxides with different reaction rates and self-assembly that can modify or even hinder the formation of pore arrays. Thermal degradation of the organic groups during thermal treatment also has to be taken into account. This is not, however, a very strict rule of thumb, because some interesting exceptions have been observed. Elimination of block copolymer templates can be achieved at $T \approx 250\,^{\circ}\mathrm{C}$. At this temperature, some organic molecules can still survive, such as fullerenes, which can be introduced as pristine C_{60} or derivatives to participate to one-pot EISA.[16,17] Some alternatives to co-condensation and grafting

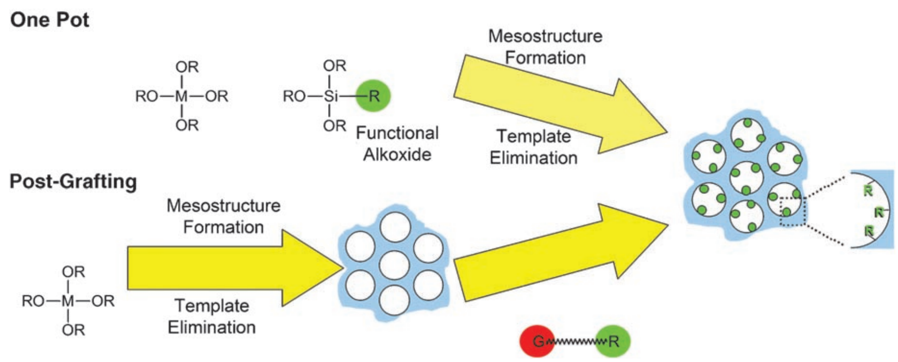


Figure 3. The main routes towards mesoporous hybrid thin films (MHTFs).

Table 1. Pre-functionalisation versus post-functionalisation.

Pre	Post
tailor compatibility R–MX_n and MX_n	tailor surface–R–MX_n interactions and reactivity
a wall consolidation step is possible for small, inert groups such as phenyl or methyl	a pre-consolidation step before grafting is possible, leading to denser and thus stronger framework walls
groups fixed on surface + embedded in the framework	groups fixed mostly on surface
functions "buried" in the framework	functions protruding into pore space
R has a role in mesostructuring (e.g., polarity, condensation catalysis, cosurfactant etc.)	mesostructure is determined before R inclusion
relatively homogeneous dispersion of R groups	pore blocking possible
limited by chemical compatibility	limited by diffusion plus pore blocking
one-pot synthesis, one or more functions, lower control of dispersion	one post-graft, one function, successive possible

methods have been also proposed. Vapour infiltration techniques have shown to be very effective in silica films in which the condensation of silica walls is still low. Exposure of a spin-coated silica film to methyltriethoxysilane vapours allowed the incorporation of hydrophobic methyl groups without reducing the pore size and increasing the mechanical strength. Another challenging route is given by an EISA synthesis that employs an organically modified alkoxide that is also acting as a template (see below).

Characterisation of mesostructured materials shows two distinctive and opposite features of thin mesoporous films: high mesoscale order associated to a very high surface area (and thus high concentration of potential functions) versus the low quantity of matter. These two aspects define the appropriate characterisation techniques for several issues. Structure and orientation are easily and accurately measurable by 2D small-angle X-ray scattering (SAXS) or 2D grazing incidence X-ray diffraction (GIXRD), even if treatment of data is a critical issue and some errors in phase recognition are quite common. TEM measurements have to be accurately interpreted to adequately support XRD data. It would be ideal to develop reliable atomic force microscopy (AFM) measurements. Surface area measurements or quantitative assessment of organic contents in thin films (by magic angle spinning nuclear magnetic resonance (MAS NMR), for example), instead, require specific setups or new developments.

A common example is the evaluation of surface area and porosity by N_2 adsorption. In most reports, these crucial data are obtained from thick films or xerogel samples by using an ordinary N_2 adsorption setup. While this is relatively easy to perform, it is not totally correct, due to the possible differences in homogeneity, pore arrangement and interconnectivity (related to inhomogeneity) found in thick samples (several microns to mm) versus thin samples (thickness <1 μm).

Film thickness greatly influences pore order and the pore system homogeneity.[18,19] This is due to the decisive effect the drying process coupled with inorganic condensation kinetics have in self-assembly, as will be shown below. This issue is crucial for homogeneity: solvent evaporation leads to an increased concentration of precursor and template. If solvent transport is not even along the sample, inhomogeneity in concentration can develop, leading to "pockets of reactivity" for the sol–gel precursors, and irregular distribution of the template concentration. Transport of solvent molecules across the film is fast for thin films, as illustrated by an estimation of ethanol diffusion. Using a simple Einstein equation ($\langle x \rangle = (D_{\mathrm{EtOH}}\tau)^{1/2}$) for a film 1 μm thick, and D_{EtOH} estimated as 10^{-5} cm^2 s^{-1} (this corresponds to a high limit), a typical diffusion time (τ) will be in the order of 10^{-3} s. These diffusion times are faster than an average condensation window (i.e., the average time that takes a concentrated system to become a gel). For 1 mm thick films, the characteristic diffusion time is in the order of the 10^3 s, which is commensurable with condensation processes. In this "thick film" case, the gelling time can be faster than diffusion and phase separation.[20] The film surface dries readily, condensation occurs and solvent is trapped in the film core, generating concentration gradients and different mesophases along the samples.[19] Any phase separation process is bound to be more irregular in thick films or xerogels than in thin films, and the former composites will often present irregularities in their texture along their thickness.

Brunauer–Emmet–Teller analysis of scratched films is tedious and might introduce errors by including some nonporous substrate fragments in the analysis due to sampling. Special cells and protocols have been designed to avoid this problem. Alternative approaches make use of X-ray diffraction (XRD) contrast techniques,[21] NMR spectroscopy,[22] or ellipsoporosimetry.[23,24] A similar kind of limitation applies to other techniques requiring important mass quantities, such as MAS NMR spectroscopy or thermogravimetric analysis (TGA/DSC). In conclusion, a robust set of characterisation techniques is needed to adequately assess order at the mesostructure, porosity, metal environment and the presence of functions in MHTFs; a "total characterisation" using a variety of spectroscopic, diffraction and image characterisation techniques is rarely found.[25]

Behind the Scenes of EISA

The thermodynamic and kinetic factors that lead to a particular phase separation and generation of mesopores are related in a complex way, and they have been discussed in detail in precedent papers.[7,13,14] However, a brief overview is necessary to position the problem and sketch the dynamics of the systems evolution.

In principle, the thermodynamic factors controlling film mesostructure, pore size and connectivity can be controlled from the outside of the system. A first approach to precisely design pore architectures is to rely on the geometry of the template (in terms of $g=V/a_o l_c$, as defined in reference [26]) or on known thermodynamic variables, such as the relative volume of the template in the final film, V_{TS},[27,28] to aim at mesostructures with different curvature. This is a fairly good approximation and V_{TS} has a useful yet elusive interpretation. The use of nonionic polymeric templates ($EO_nPO_mEO_n$, in which $EO = -CH_2CH_2-O-$ and $PO = -CH_2(CH_3)CH-O-$) with the same hydrophobic tail ($m=70$) and hydrophilic headgroups with different volume, such as P123 ($n=20$) or F127 ($n=106$) results in 2D hexagonal or *Im*3*m* cubic mesostructures, in most cases.[25] When P123 is used in low concentrations, the final mesostructure is *Im*3*m* cubic with high curvature; increasing the P123/metal ratio (and therefore the V_{TS}) leads to 2D hexagonal mesostructures. Therefore, many research groups have used template/alcohol/water phase diagrams as an approximate guide to success, considering that Si–OH groups are roughly equivalent to water.[29] However, even if the trend is right, there are basic things that remain unexplained, such as the great variety of cetyltrimethylammonium bromide (CTAB)/silica mesostructures (which can have four phases—$p6_3/mmc$, *Pm*3*n*, *p*6*m* and lamellar—instead of the only *p*6*m* hexagonal phase reported[30]), or the exact boundaries between different phases or the real meaning of a parameter such as V_{TS}. Recently, synthesis routes have been developed in which the accent is put in using polymeric surfactant templates with a greater solubility difference between the hydrophilic and hydrophobic domains. This approach is useful to enforce organisation in complex oxides.[13,31]

Water contents in the system or the hydrolysis degree of the inorganic species have been proved important features,[4,28] as they can enhance the formation of ordered micelle arrays, and control the interactions between the template and the inorganic network that take place at the hybrid interface. It is clear that more accurate diagrams taking into account these factors are needed. The Sanchez group recently introduced a quaternary "texture diagram", in an attempt to better explain and locate these stability domains.[7] In summary, the relevant thermodynamic factors are more or less understood, even if not totally explained. Basically, packing interactions and compatibility at the hybrid interface open the possible doors towards order at the mesoscale. Nonetheless, kinetic factors will have their starring role and will determine the path towards organisation.

From solution to fresh films, "a race towards order": The evolution of an EISA system along time (i.e., the kinetics of the system) can begin to be understood when a system trajectory is plotted in the phase diagrams containing the main actors of the system. If the concentration of the inorganic and template species in the initial dilute solutions is low, no liquid crystalline species will be formed; even micelle formation is difficult under these conditions, because the critical micelle concentration (*cmc*) of the template in the solvent (often a mixture of low weight alcohols and lower water quantities) is relatively high. When solvent evaporates, the self-assembly properties of the template enter the scene, and aggregation processes (i.e., micellisation) begin to take place (Figure 4a). When higher concentrations are reached, a liquid crystalline phase is formed, due to micelle aggregation. In the ideal case, micelles pile up in ordered structures and the inorganic building blocks locate themselves in the outside (polar) fraction of the organic liquid crystal formed. A hybrid mesostructure (inorganic skeleton surrounding an organic liquid-crystalline phase) is thus formed. A scheme of the process occurring in a thin film and its correlation with a simple ternary phase diagram is shown in Figure 4b.

In-situ SAXS experiments coupled with interferometry shed light into these complex assembly processes.[32–35] In most of the cases, the mesostructure appears after the

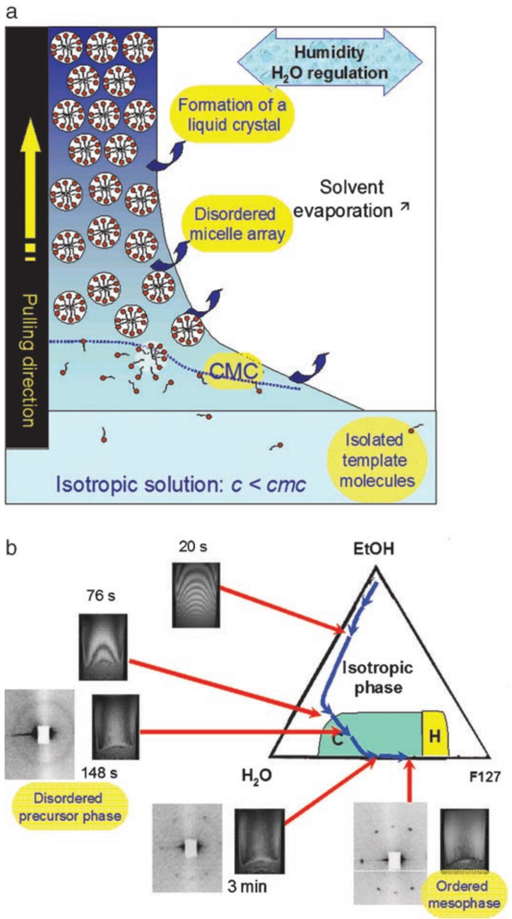


Figure 4. a) Scheme of the formation of a thin mesostructured film upon dip-coating, adapted from reference [14]. b) Simplified system trajectory of the formation of a mesostructured TiO_2 film plotted along a ternary diagram nonionic surfactant (F127)/ethanol/water. Typical interferometric and SAXS patterns are shown for each point.

drying line (i.e., when practically all the solvent has evaporated and the film attains more or less its final thickness). Two slightly different behaviours have been so far reported. In the case of cationic surfactants such as CTAB, well-defined mesostructures are formed upon drying, and a number of phase transitions have been reported between them, until reaching a final mesophase.[35,36] This multiplicity of mesophases upon mesostructure formation has been observed by in-situ X-ray reflectometry experiments on silica/cationic surfactant films grown at the air–water interface.[37] In the case of nonionic templates, the formation of a short-range-order phase (sometimes called a "wormlike phase") precedes the formation of an organised and well-oriented product mesophase. This kind of "disorder-to-order" transition has also been observed in the initial stages of formation of thick films or xerogels.[38] When seeking a well-defined organisation at the mesoscale, the system has to be designed to phase separate and organise completely before the medium becomes rigid enough to "freeze" a disordered phase, or even to "freeze" before any phase separation, leading to a nonmesoporous, or poorly ordered film. In other words, the "race towards order" must be won.[13] Given that the thermodynamic differences between ordered or disordered mesophase are not significant at ambient temperature,[39] this is only possible if 1) the nucleation rate for an organised mesophase made upon the self-assembly of micelles and inorganic counterparts (i.e., the NBBs of the hybrid mesophase) is important and 2) the medium is compliant enough to permit rearrangement of the NBBs (see below). A too viscous medium, or an inorganic network with a high rigidity due to cross-linking will be deleterious in order to obtain organisation. The kinetic phenomena involved in the "race towards order" (Figure 5) are analogous to those involved in phase separation at the micron scale.[40]

In summary, film formation by EISA is a "chemical symphony" that implies the coordinated interplay of the following phenomena:

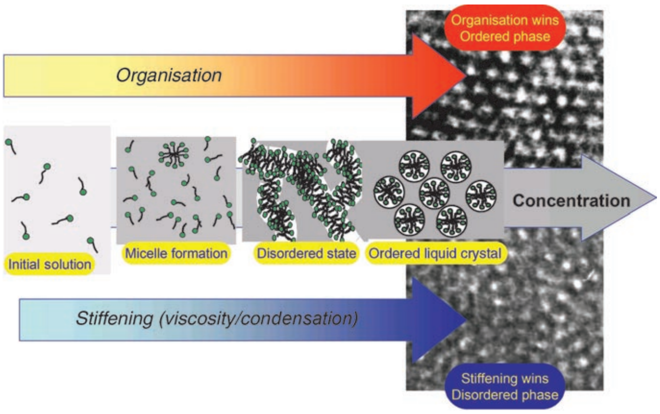


Figure 5. Scheme of the "race towards order" concept. The forces leading to order are predominantly thermodynamic ones (i.e., optimisation of self-assembly). Film stiffening due to a viscosity increase (by concentration or by inorganic condensation) may "freeze" the disordered intermediate mesophase.

1) Sol–gel chemistry (shape, size, hydrophilicity and connectivity of the inorganic or hybrid NBBs).
2) Self-assembly between template molecules, to form micelles, between micelles, to form extended liquid crystalline domains, and between micelles and inorganic or hybrid NBBs.
3) A "race towards order" in which the processes of gelling and order from phase separation compete.
4) Mass transport, which controls the homogeneity of the processes (and thus the mesostructure) along thickness.

These are the most important factors to take into account for one-pot synthesis. Surface functionalisation issues (surface chemistry etc.) will be of utmost importance in the case of post-grafted MHTFs, and will be discussed later on.

Flexibility leads to success in ordering: An important feature of EISA-obtained mesostructures is the "flexibility" of the framework after a film has been deposited. The importance of this framework flexibility for a successful organisation has been postulated in earlier papers,[14,37] and recognised in several works. In-situ studies of fresh block-copolymer-templated TiO_2 thin films show that water uptake or release in or out of the film can swell the mesophase, or can even change it from, for example, $Im3m$ cubic to $p6m$ 2D-hexagonal phases.[25] Analogous experiments in EISA-derived thick films show that ordered phases can be obtained from TiO_2–template phases that initially do not present any order at the mesoscale.[41] In the case of silica–CTAB mesostructured thin films, in-situ SAXS experiments performed by Cagnol et al. showed that the initially obtained mesostructure of a freshly synthesised film can be modified by changing an external parameter, such as humidity.[42] This flexibility means that the framework walls are not rigid, due to a low extension of inorganic condensation at this stage.[43] At this stage we could even talk about framework NBB loosely bound to each other (Figure 6).

In silica films, there is enough experimental evidence of formation of cyclic species[35,44] (four- or sixfold silica rings) that can be considered as a kind of NBB that form the pore walls. Control of inorganic condensation is accomplished by tuning the sol–gel chemistry of the metal–oxo couple in the initial solutions. In the case of transition-metal centres, low pH values suffice to hinder M-O-M condensation, leading to low size molecular clusters.[25] The control of Si-O-Si condensation is slightly more complicated, and pH and aging times have to be optimised to yield the most favourable condensation rates in order to obtaining an organised mesostructure.[7,19a,c]

Some clues of the condensation kinetics can be obtained by applying in-situ spectroscopic techniques, such as ATR-FTIR spectroscopy,[35] FTIR ellipsometry[45] and IR synchrotron radiation. In this case timescale is very important and the experiments not very simple to perform, because of highly overlapping signals from the different species participating in EISA. Ethanol and water vibrational modes over-

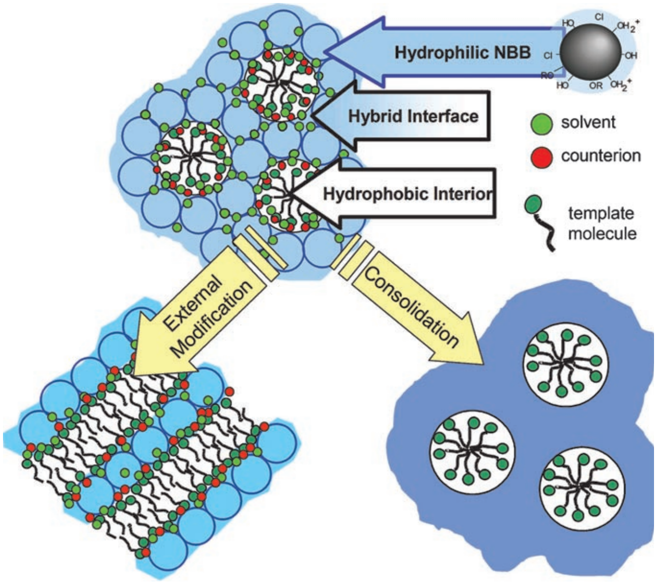


Figure 6. Scheme of a fresh MO_2/template thin film formed by an assembly of the framework nano building blocks (NBBs) around an assembly of micelles. The colloidal metal–oxo NBB result from partial sol–gel condensation. These NBB present a hydrophilic surface, due to ≡M-OH and ≡M-OH_2^+ groups. Solvent evaporation enables the formation of a flexible liquid crystalline phase. The whole structure is uncondensed, and has to be further consolidated by co-condensation between the framework NBB. External solicitations (for example, a change in the external humidity, eliminating solvent) may lead to a phase change.

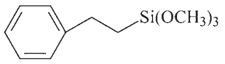
lap and shadow the signal from Si-O-Si and Si-OH at the first stages of film formation.

Film consolidation and template elimination: The fresh film (low-condensed molecular species plus template and remaining solvent) is liquid-like enough to allow rearrangements, and therefore is readily soluble in solvents such as alcohols or water. A consolidation step is often needed, in which inorganic condensation is encouraged (e.g., by moderate thermal treatment, $T > 150\,°C$, or alkalinisation by exposure to NH_3 vapours). These treatments produce a densification of the pore walls, and a uniaxial contraction. As a result, the pores end up with an ellipsoidal shape. Consolidation treatments are very important, and need to be reproducibly performed. Residual wall porosity can be eliminated in a controlled fashion, and the crystalline nature of the inorganic wall can be tailored by an adequate set of post-synthesis conditions. In transition-metal-derived thin films, treatment conditions can be set to create open porosity, therefore improving pore accessibility.[46] In the case of methyltriethoxysilane (MTES)-derived MHTFs, a carefully designed consolidation–calcination sequence permits to obtain isolated spherical mesopores with no microporosity. Fresh films present a flexible network due to the low condensation of MTES; a slow temperature ramp allows rearrangements and micropore closure. Further thermal treatment results in template elimination and closed mesoporosities. Methyl functions are robust enough to be conserved until 500 °C.[47]

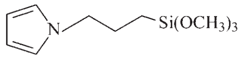
Thermal treatment has severe limitations in the case of most MHTF derived from one-pot routes, as the desired functions can be partially or totally eliminated. For this kind of film, template extraction must be performed in conditions mild enough to keep the integrity of the inorganic network (i.e., slightly acidic alcohol/water mixtures).

The Production of Hybrid Organic–Inorganic Films

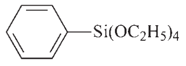
The increasing interest of MHTFs is in great part due to the possibility to add tailored properties to the films through the presence of specific organic groups (a selection of which is shown here). Applications of high technological interest and a very large economical impact are expected in microelectronics (low *k* dielectric materials), photonics (low refractive index materials) and sensor industries (gas and humidity sensors). Most of the synthesis procedures for MHTFs have been devoted to add new functions keeping in mind the final application. Low *k* dielectrics has been the most studied application for MHTFs right now. This is also the only MHTF type with a set of experimental data that are comprehensive enough to allow a reasonable comparison between the proposed innovations and the competing materials. We have, therefore, devoted a specific section to this subject, which has been used as a case study.



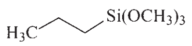
(2-Phenylethyl)trimethoxysilane



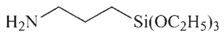
N-(3-Trimethoxysilylpropyl)pyrrole



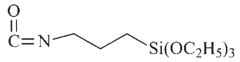
Phenyltriethoxysilane



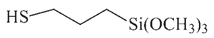
n-Propyltriethoxysilane



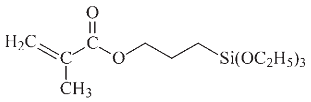
3-Aminopropyltriethoxysilane



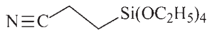
3-(Isocyanatopropyl)trimethoxysilane



3-(Mercaptopropyl)trimethoxysilane



Methacryloxypropyltriethoxysilane



2-Cyanoethyltriethoxysilane

$H_3C{-}Si(OC_2H_5)_4$

Methyltriethoxysilane

It is also very relevant to establish as much as possible a clear path to the synthesis/processing/structure/property relationship for MHTFs; this basic tool is needed to reach an advanced comprehension of these new fascinating materials.

Structure and self-assembling kinetics in methyl-containing hybrid films: Films prepared by one-pot cohydrolysis of tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) are a simple route to mesostructured materials with low *k* values. However, these materials show other interesting properties, one of which is a high level of organisation of the porosity. It should be observed, in fact, that the self-organisation, in general, generates organised domains, similar to crystalline grains, and the organised porosity is rarely extended within all the film thickness and in ranges of millimetres. In a recent work, Kuroda et al.,[48] obtained silica self-assembled films the order of which extends through a range of centimetres. The result was obtained by preparing an oriented polyimide layer on the silicon substrate to allow the growth of highly ordered mesostructures during film deposition. This technique, on the other hand, cannot avoid structural defects such as stacking faults. A simple one-pot deposition of hybrid MTES–TEOS films can produce, instead, highly ordered defect-free materials, even if the order has a shorter range. It is interesting to observe that highly ordered MTES–TEOS films have been obtained by several authors;[51,53,81] even if the recipes that have been employed are a little different, the materials showed in any case a high organisation. Identification of the mesostructure is in general not very simple, and in literature some inconsistencies are quite common. The identification is complicated by the phase transformation induced by the post-deposition thermal treatment, which is done to remove the template and to condense the pore walls.[49,50] Even if this effect is well recognised, a clear identification of the phases that are involved in the transitions is seldom reported.[49] This is due to the difficult interpretation of SAXS patterns and to the lack of a codified procedure to achieve phase identification in the case of mesostructured films. Mesostructured MTES-derived silica films have been observed to give a body-centred tetragonal mesostructure by Yu et al.,[85] and a tetragonal *I*4/*mmm* (in the space group) mesostructure by Falcaro et al.,[51] in the case of mixed MTES–TEOS films. The thermal induced shrinkage in the film causes a change in the cell parameters, but the phase evolves retaining the same symmetry throughout a wide range of temperature of calcinations (Figure 7).[52]

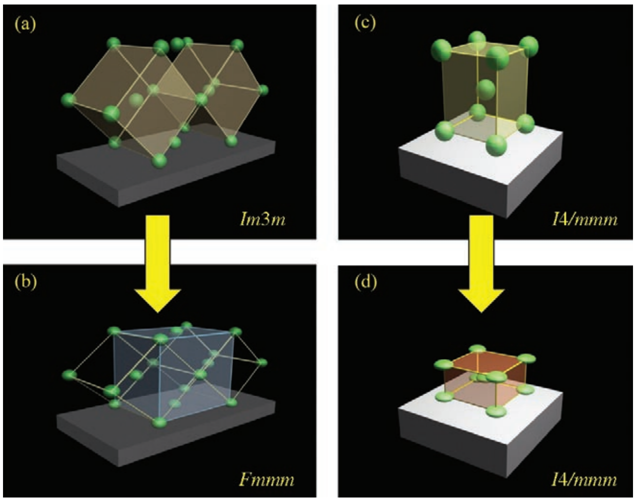


Figure 7. Phase transitions observed in dried (60 °C) TEOS (a) and MTES-TEOS (c) films and upon calcination at 600 °C (b and d, respectively).

The structural difference between silica and hybrid silica/MTES films implies a fundamental difference in symmetry and in the thermal evolution. The presence of the methyl groups seems to be very important during self-assembly, modifying the packing of the micelles and the interconnectivity of the pore walls, which remains more compliant for a longer time to reduce stresses in the films. An in-situ experiment, using infrared light, has allowed the clarification of the kinetics related to water–ethanol evaporation and silica polycondensation during EISA of cast films.[53] The evaporation of water has been observed to take place in three different phases, with a first rapid evaporation followed by an increase in H_2O content and a second evaporation stage. A comparison with silica EISA films has allowed the deduction that the polycondensation of silica is highly slowed down in presence of hydrophobic methyl groups resulting in a very high degree of order in the final mesostructure. The "race towards order" produces an organised structure only if the kinetic constants of the process follow this hierarchy [Eq. (4)],[54,55] with k_{inter}, k_{org} and k_{inorg} being the relative rates for interface formation, organic array assembly and inorganic polycondensation, respectively.

$$k_{\text{inter}} > k_{\text{org}} > k_{\text{inorg}} \qquad (4)$$

The comparative in situ study by FTIR, between evaporation–polycondensation kinetics in silica and hybrid films, supports therefore the idea that the silica polycondensation rate is a basic parameter for EISA. The IR measurements show, in fact, that longer polycondensation kinetics leads to a better and easier self-organisation of the mesostructure.

Other examples of hybrid mesoporous films synthesised by means of one-pot routes: One-pot self-assembly of MHTFs has not, however, been restricted to MTES–TEOS compositions, even though the high practical interest this system has attracted most of the attention of researchers. Other systems have been also investigated and mesostructure hybrid films of different compositions have been reported. It should be noted though this route has its main interest in the possibility of adding a specific organic functionality, the one-pot synthesis also clearly affects the final pore structure and the kinetics of self-assembly. Ogawa and Kikuchi[56] observed that cohydrolysis of vinyltriethoxysilane with trimethoxysilane (TMOS) slows down the TMOS condensation giving a highly ordered thicker film (> 10 μm). Cagnol et al.,[57] with a systematic approach, investigated the effect of the organic functions on the MHTF mesostructure; 2D hexagonal or cubic mesophases were observed as a function of water/alkoxide ratio and the amount of surfactant, even if a comprehensive understanding could not be yet depicted. The same group observed that the R function could act as a co/surfactant.[58] An important modification of pore surface is achieved employing amine groups, the presence of which is very useful in several applications; a first report of this synthesis has been done by Brinker[59] and co-workers who described a one-pot EISA route to obtain, by using a block copolymer (Brij 56) as a structure directing agent, MHTF with $-NH_2$ functional groups. TEOS was cohydrolysed with an organically modified alkoxide bearing an amine functionality, 3-aminopropyltriethoxysilane (APTES), and to avoid the catalysis of TEOS by the basic $-NH_2$ groups a neutralising pre-reaction of $-NH_2$ with a strong acid was employed. The organic template was removed by an acidic solvent extraction that left the amino functional groups on the pore surface. Another example of MHTF films reported by the same group[60] is the synthesis of highly ordered mesoporous thin films with $-COOH$-terminated pore surfaces. The $-COOH$ groups, which are negatively charged in neutral to basic media, are used in the development of inorganic ion channels. In contrast, $-NH_2$ ligands, which are similar to $-COOH$ ligands, but are positively charged in neutral to acid media, can be used both as binding sites for enzymes, antibodies and other proteins and create an electropositive environment that can eventually control anion transport.

The presence of functional groups is very important in the fabrication of nanoreactors; for example, the preparation of gold nanowires within the pores of mesoporous silica thin films, the pore surface of which is functionalised by reacting the silanols with APTES.[61] The immersion of the $-NH_2$ functionalised MHTF in aqueous solutions of $HAuCl_4$ leads to the formation of highly dispersed gold nanowires by means of a neutralisation reaction.

From mesostructured films to nanocomposites: A nice exploitation of the potential of mesostructured films is offered by the possibility to build up new families of hybrid nanocomposites through EISA.[62] The porosity of the films is an organised host space in which incorporation of different types of organic polymers allows the preparation of new nanocomposites with enhanced properties. An interesting example is the fabrication of a silica–poly(2,5-thienylene ethylene) (PTE) hybrid mesostructured film through EISA. The main problem connected with this approach is how to achieve polymerisation of the organic monomers after their incorporation in the pores. In this specific case the use of a one-pot polymer synthesis to prepare PTE by means of a palladium-catalysed polymerisation of aryl diodides with acetylene gas in aqueous media[63] lead to mesostructured hybrid films containing conjugated polymers.

Self-assembly without surfactants: The possibility to achieve self-assembly without surfactants is a very attractive one. Self-organisation, in this case, is based on the specific design of the molecular building block precursors with self-organisation capabilities. Shimojima and Kuroda[64] have synthesised siloxane-based oligomers with an alkyl chain bonded to a silicon atom bearing three branched trimethoxysilyl groups ($C_nH_{2n+1}Si(OSi(OCH_3)_3)_3$, $n=10$ or 16). Controlled hydrolysis and polycondensation of this precursor formed lamellar or 2D-hexagonal mesostructures, fabricated as cast or spin-coated hybrid organic–inorganic films.

The evident advantage of this strategy is to avoid employing the surfactant; this simplifies the synthesis and cuts the final step of surfactant removal. On the other hand, this route is restricted to silica hybrids, because of the hydrolytic instability of the bonds between transition metals and carbon. This is a further element of rigidity, because pore surface functionalisation is conditioned by the presence of the alkyl chains. Notwithstanding, it is an elegant and challenging new route for the fabrication of hybrid organic–inorganic mesostructures. It should be also observed that attempts to achieve self-assembly by co-condensation of alkyltrialkoxysilane with TEOS[65,66] never produced well-defined block oligomeric precursors, which seems an essential step to obtain mesostructures with a higher degree of order without employing surfactants. Hydrolytic reaction of *n*-alkyltriethoxysilane with various chain lengths ($C_nH_{2n+1}Si(OC_2H_5)_3$, with $n=8$, 10, 12, 14, 16, 18) in ethanol gave, in fact, only multilayered dip-coated films, the interlayer structure of which depends on the alkyl chain length.

Post-functionalisation approach—examples of silica and non-silica systems: In the post-synthesis methods presented above, the organic molecules diffuse through the pore network and react with the pore surface, yielding a MHTF. These bifunctional molecules (denoted R–G) contain the desired R function and a suitable grafting group (G = alkoxysilane, phosphate, carboxylate, etc.), which is able to attach to the metal centres located at the pore surface. The anchoring of the G group is driven by condensation (in the case of silanes on silica or titania), or by complexation (in the case of a G group able to complex a transition-metal centre).[67] Grafting can be thus covalent (practically irreversible) or coordinative (partially reversible). While stronger grafting groups are needed for sensing and catalysis (i.e., function stability and repeatability), more labile functions are also interesting in the quest for controlled delivery or reversible signalling. The grafting strength will be also important for the even incorporation of the R function along the pore systems.

Two key factors that control the homogeneous incorporation of organic functions in thin films are 1) the accessibility of the pore system (including molecule diffusion to the whole film) and 2) the reactivity of the R–G molecules towards the surface or among themselves. The first factor will essentially depend on the possibility of pore interconnection, and the symmetry and orientation of the pore mesostructure. For example, in F127-templated TiO_2 or ZrO_2 mesoporous films, it has been observed that the uptake of long-chain dialkyl phosphates is faster in an *Im*3*m* cubic mesophase than in a *p*6*m* 2D hexagonal one. This difference was attributed to the presence of pores open to the surface in the cubic phase that were absent in the *p*6*m* mesostructure.[67b,68] Moreover, the pores in the cubic phase are interconnected due to the development of large size necks upon thermal treatment and shrinkage of the original mesostructure.[69] Shrinkage of the *p6m* system results in tubular pores of elliptic section, but no new pore interconnections are created, and molecules have to diffuse from pore to pore through defects in the mesostructure (e.g., boundaries between organised domains). Pore blocking during post-functionalisation can also occur. This phenomenon has been well described in the case of hybrid silica powders.[70] Organosilanes entering a pore can readily react with the silica surface, and attach in an irreversible fashion, accumulating in the pore entrances and hindering diffusion of similar molecules to the innermost pores. The condensation chemistry of organosilanes has to be controlled: these molecules can react among themselves, apart from reacting with the surface. This can also lead to partial pore blocking, due to the formation of $(RSiO)_x$ polymers inside the pore space. The possible post-functionalisation routes presented above have been less used than one-pot procedures to generate silica MHTFs; however, these post-synthesis routes have been successfully applied to modify several non-silica oxides, in which the relatively reversible G−M bonds help to attain homogeneous distributions throughout the films.[68]

Access to a second chemical entity—sensors, separators, guest molecules and multiple functions: An important feature of MHTFs is the accessibility of other molecules or ions to the modified pore system. While detailed work has been performed on this issue for hybrid mesoporous powders,[5,71] no systematic work has been yet performed in the nascent MHTF field, as the majority of the current studies are focussed in the characterisation and the construction of the hybrid porous framework. However, recent work shows that MHTFs are further accessible to ions or organic molecules, paving the way to selective sensors, preconcentrators or exchangers.[8,58,68,72,73] Indeed, a careful control of the attached function permits tuning of the diffusion of a variety of molecules within the pore network, and permits the synthesis of MHTFs that respond to an external stimulus. A remarkable recent example is an azobenzene-modified silica mesoporous framework. Irradiation with visible light permitted optical switching of the *trans* or *cis* conformation of azobenzene, which controlled the effective pore size and, correspondingly, the transport behaviour of guest molecules. Thus, it was possible to tune mass transport of iron complexes by photoregulation.[8]

The accessibility of a pore system and the presence of different surface species can be exploited to create MHTFs that carry more than one organic function. A recent example exploits the occurrence of surface sites with different reactivity to generate bifunctional MHTFs. In the first step, a hybrid $M(RSi)O_2$ MHTF (M = Ti, Zr etc.) is created by one-pot co-condensation of MCl_4 and $RSi(OEt)_3$. The R function can partially block some surface sites. The second function R′ is added by post-synthesis treatment with an organic R′–G molecule, in which G is a complexing group, able to selectively attach to the Ti or Zr sites, which are freely accessible (Figure 8a). In these double functional systems, the R′ function can be firmly or loosely attached, depending on the strength of the G–M interaction.[72]

The examples cited above give an idea of the "pore engineering" that is currently possible in MHTFs. Inclusion of molecules of biological interest, from enzymes to genetic material is a relatively straightforward step. Several strategies should be explored that are already implemented for surfaces, polymers or even mesoporous hybrid powders and permit the precise positioning of functional groups in an accessible cavity (Figure 8). These strategies will certainly enrich the library of pore features with complex selective systems that can have molecular imprinting and/or interacting functions, just as in the case of the natural cavities of an enzyme. Another challenge is the design of multilayered MHTF-based systems bearing different sets of accessible functions that can mimic a natural system (controlled behaviour in a given environment, response to stimuli, transfer of chemical information etc.). These complex systems with a huge density of different functions with perfectly defined locations in space can build up the interface between electronically driven devices and living organisms (i.e., "bio-wiring").

Structure–property relationships in MHTFs: A deeper knowledge of a material is truly achieved only when the synthesis–structure–property relationships have been extensively studied and understood. The lack of systematic data on this issue, at this stage of still pioneering work on MHTF, does not allow for a comprehensive understanding; however some trends are clearly emerging. The mechanical properties of MHTF have a fundamental importance to develop future successful applications, and include a set of different values to be measured as a function of synthesis, processing and film composition. In particular, residual stress is very important to integrate the film production in silicon technologies; the data available at the moment show that a significant reduction of residual tensile stress is observed in MHTFs and that this reduction is a function of the fraction of organic moieties present in the film composition. This can be a good reason to select a MHTF instead of a purely inorganic mesostructured film for several types of applications in which thermal stability is not a critical issue. In general, the pore thickness and the introduction of silsesquioxanes silica species, (the Si−C−C−Si bond is more rigid than the SiO_2 one[74]) affect the mechanical properties, enhancing the elastic modulus. CTAB-templated MHTFs have pores of smaller dimensions relative to nonionic surfactant-templated MHTFs; this property is at the expense of a lower pore-wall thickness and a lower mechanical stability.

Another advantage is the control of the hydrophobicity–hydrophilicity property. The same organic functions that reduce the residual stress in the films play also an additional function by enhancing hydrophobicity through methyl or organo-fluorinated groups.[75] The refractive index changes according to porosity and *k* values; higher porosities give a lower refractive index, which is a much desired property for photonic applications. However, this property can be adjust-

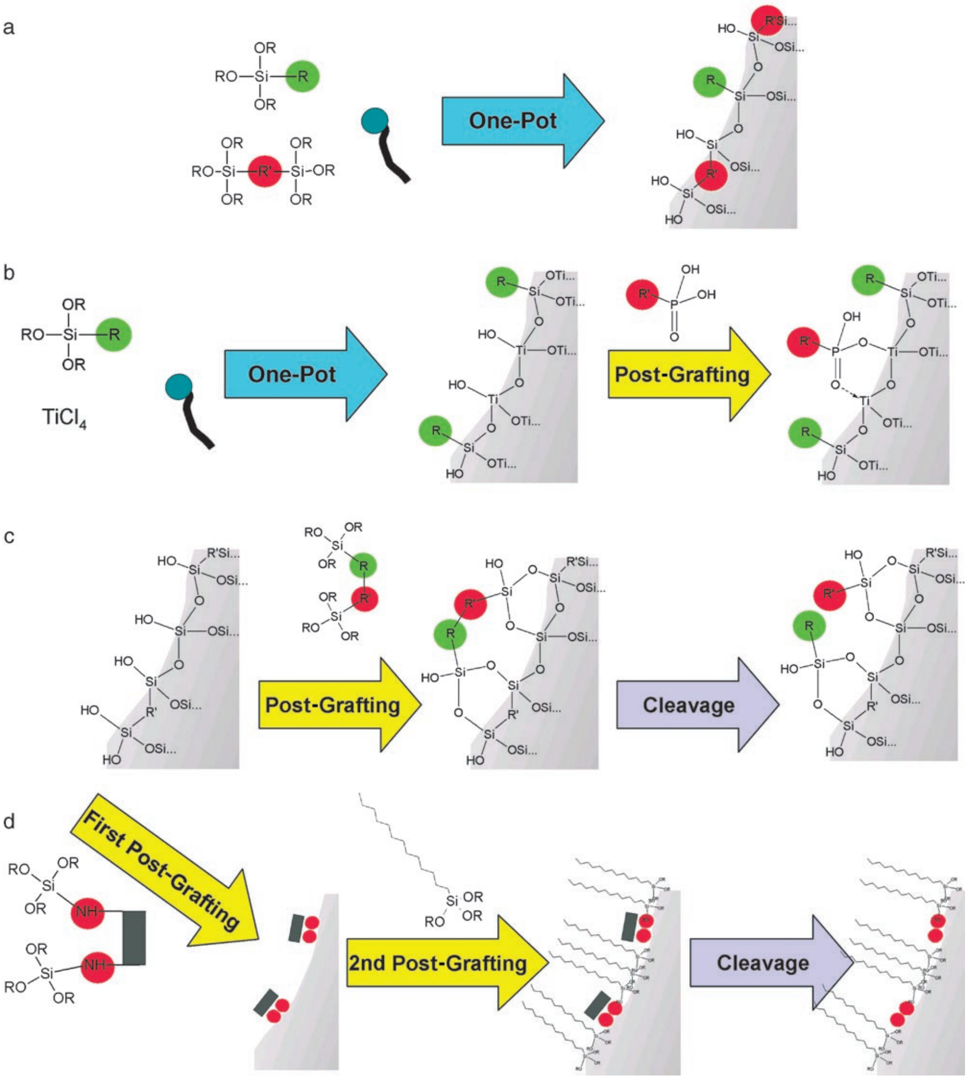


Figure 8. Different synthesis strategies to achieve "pore engineering", by selectively locating organic functions within walls or on a pore surface: a) one-pot synthesis using two different organoalkoxides (reference [9]), b) one-pot synthesis followed by post-grafting on the remaining surface sites (reference [72]), c) post-grafting of a bridged function, followed by cleavage and exposure of the new functions (reference [94]), d) double post-grafting followed by cleavage, leading to functional cavities with defined size and shape (adapted from reference [71]).

ed not only through a porosity control, but also by using different compositions of MHTFs. Introducing fluorinated groups can further reduce the refractive index, increasing the hydrophobicity, without the need of reducing the porosity at expenses of mechanical stability. Apart from this "macroscopic" hydrophobicity effect, organic functions at the interior of pores have the potential to control the accessibility and the diffusion of molecules present in solution. In an extreme case, MHTFs supported on an electrode carrying adequately functionalised pores should be capable of generating a partition or preconcentration of a selected solute, therefore paving the way to creating robust selective membranes for analytical or decontamination applications.

Applications of MHTF, a case study—hybrid mesostructured films as ultralow *k* dielectric materials:[76] The increasing miniaturisation of integrated circuits poses a severe challenge to the semiconductor industries to search for new materials that can be integrated into the system architectures. The increased density of transistors and wires per unit area requires ultralow *k* dielectric materials to avoid problems due to interconnect resistance–capacitance delays, signal crosstalk and power consumption.[77] Following the International Technology Roadmap for Semiconductors 2001, the next generation of dielectric materials for a successful integration at the 65 node technology, which is expected to be in production for 2007, needs effective[78] *k* values in the 2.7–2.3 range.

New materials with ultralow *k* values should also comply with several very strict requirements to be integrated with the performance specifications necessary in the microelectronics industry. In particular, the compatibility with the damascene processing[79] and its related requirements is fundamental. The material design must be done by evaluating the mechanical properties: elastic modulus, hardness and residual stress in the film; the thermal stability; the etching capabilities to allow chemical mechanical planarisation;[80] the hydrophobicity; the adhesion and the control of thermal expansion coefficient. Porosity is, therefore, just one the many properties to be controlled and a very careful engineering of the low-*k* material has to be done.

Different strategies have been employed to synthesise mesoporous films with a hydrophobic surface; in the majority of the cases, methyl groups have been used to obtain hydrophobic hybrid mesoporous films. The presence of water increases the *k* value and can affect the thermal stability of the silica films.[81,82] The syntheses have been also addressed, in general, to allow deposition by spin-coating and to fabricate films in which mechanical and thermal stability are improved.

The simpler approach to add hydrophobicity to the mesopores is to functionalise the surface with methyl groups by the three main methods cited above. The most common approach to remove the residual surface silanols to make the material hydrophobic is the reaction of the silanols in thermally calcined silica films, with hexamethyldisilazane (HMDS) or trimethylchlorosilazane (TMCS) in a post-synthesis treatment. Vapour-phase reaction of HMDS has shown to be very effective in removing the silanols and lowering the dielectric constant.[83] Other alternative routes have been proposed, such as in-situ derivatisation of the precursor solution with TMCS,[84] self-assembly with diblock copolymers and MTES to obtain pore isolation,[85,86] co-hydrolysis and self-assembly of methyltriethoxysilane (MTES)/tetraethyl orthosilicate (TEOS) mixtures (one-pot EISA) and MTES vapour infiltration techniques.[87] The groups of Watkins[88] et al. and Balkenende[89,90] et al. have, however, demonstrated the compatibility of integrated circuit (IC) devices with mesoporous hybrid films by using two different routes. In spite of the different measurement techniques and the unavailability of full sets of data, there are some critical comparisons that can be useful to address. The method proposed by Watkins et al. to fabricate ultralow *k* mesoporous hybrid films is based on an innovative process by which the films are prepared by infusion and selective condensation of silicon alkoxides within microphase-separated block copolymer templates that are dilated by supercritical CO_2. In a typical preparation a film of surfactant is spin-casted on a SiC substrate and immediately after the template is infused with a solution of MTES–TEOS in CO_2 at 60 °C and high pressure. The precursors diffuse into the template, which is weakly dilated by the super critical fluid. A selective condensation within phase-separated acidic hydrophilic domains is obtained. Only the rapid extraction of the alcohol produced by the condensation of the alkoxides promotes the polycondensation and the network formation. Detemplating is done in H_2–N_2 plasma and the residual silanols are finally capped by reaction with HMDS. The mesoporous films exhibit $k=2.2$ and a high integration with the IC technologies. This process is, however, a kind of "controlled-assembling" process, even if is giving mesoporous organised hybrid films, because the templates are forced to organise before the network is formed. This is also giving the advantage that compatibility in solution between the templates and the precursors is no longer a strict requirement. On the other hand this technique is potentially more expensive and requires more fabrication steps.

Table 2. Dielectric constants and pores size in various MHTF prepared for low *k* dielectric applications.

Processing	Dehydroxylation	Pore size [nm]	Dielectric constant (at 1 MHz)	Reference
TEOS+MTES+MPTMS	closed pores	8	1.9	[92]
polyoxyethylene ether	HDMS	5	1.8–2.5	[83]
TEOS + TMCS Pluronic P123	HDMS	4–8	1.42–2.5	[84]
TEOS + MTES		3 (CTAB)	2	[89]
Brij76, Pluronic	HDMS	6.5 (Brij76)	1.7	[89]
F127, CTAB		8 (F127)	1.8	[89]
TEOS + MTES	HDMS		2.2	[88]
Brij, Pluronic F108		–		[88]
TMOS + bridged silsesquioxianes CTACl		–	1.9–4	[93]

The route of Balkenende et al. is based on a classic one-pot EISA synthesis of hybrid films prepared by co-hydrolysis and self-assembly of an MTES–TEOS mixture. The introduction of pendant methyl groups by the one-pot route has the advantage that it is simple but also more effective, because the hydrogen-bonded surface silanols are very much sensitive to the grafting reactions[70,91] and a fully hydrophobic pore surface is more difficult to achieve.

The first important feature to be addressed to produce hybrid films with the desired dielectric properties is the control of volume porosity and pore dimensions, related to the choice of the surfactant (see above). Ionic surfactants produce pores of smaller dimensions compared to nonionic block copolymers, but the resulting films are also mechanically less robust, because of the thin pore walls.[90] In general, the *k* value in block copolymers, even if the pores have larger dimensions, is low enough to give a good compromise in terms of dielectric and mechanical properties. An overview of the main results obtained for MHTFs as ultralow *k* dielectric materials is shown in Table 2. Values of the dielectric constant lower than 2, that is, enough to satisfy the 65 node technology, are reported for all the materials. The results from reference [92] refer to mesoporous but not organised films and can be used for a comparison.

An important requirement for films to be applied in ICs is the control of residual stress that can induce adhesion failure with substrate and fracture. If the residual stress is above the 50–100 MPa, curvature of the wafer substrate can be observed with several problems in handling the wafer in a vacuum chunk. The nature of the residual stress in the films is tensile and originates through film shrinkage during drying and annealing. Immediately after the deposition by spin-coating the stress in the film is relatively low, because the silica network is not completely formed and there is enough compliance in the material to keep the stress low. With the advance of the polycondensation reactions, the silica network becomes more rigid and stress arises. It is interesting to note the different behaviour of MTES–TEOS films; the presence of methyl groups decreases the connectivity of the silica matrix lowering the elastic modulus and the residual stress. This effect has been observed in self-assembled MTES–TEOS hybrid films by different authors.[85,90] The important role of methyl groups to decrease the stress is clearly observed from the data in Figure 9 (adapted from reference [90]), in which the stress before and after film annealing is reported as a function of the MTES content in the precursor sol. Wu et al., in particular, have analysed in detail the strain and strain relaxation in EISA MTES–TEOS films and correlated them to the formation of dislocations in terms of linear defects within the organised porous hybrid films.

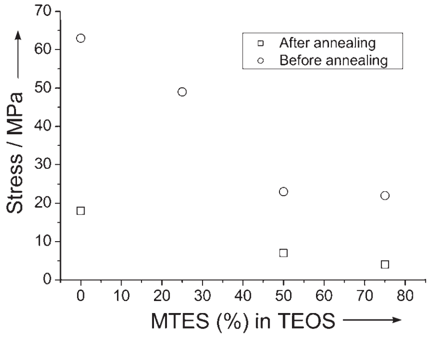


Figure 9. Film stress before (circles) and after (squares) film annealing as a function of the MTES content in the precursor sol. Adapted from reference [90].

MTES–TEOS systems are not the only possible solution for low *k* dielectric applications. An alternative is represented by hybrid films prepared by using a mixture of silica alkoxides (TMOS) and silsesquioxanes precursors, $(RO)_3$-Si-R′-$(OR)_3$ with R′ being a bridging organic group. The measured dielectric constant is in the range of MTES–TEOS samples, but the level of organisation appears lower and the materials properties is not significantly improved.[93]

Concluding Remarks

In the last five years, considerable progress has been made in the synthesis and characterisation of tailored pore MHTFs, which remain a promising class of nanomaterials, offering a wide range of potential applications. One-pot or post-grafting synthesis methods permit the synthesis in one or two steps of a finely tailored material that has controlled features such as pore size, pore shape, surface area, wall composition, surface characteristics and many more. The chemical paths involved in these syntheses are beginning to be understood, thanks to exhaustive studies, including in situ techniques. In principle, thermodynamics of the template–solvent–water system (i.e., using ternary diagrams to predict a given mesophase) gives a reasonable first-order approach to the possible final phase obtained. Some thermodynamic features can be exploited to improve ordering; for example, selecting a template with a substantial difference between the hydrophilic and hydrophobic domains. However, kinetic effects are also crucial. The complex interplay of the rates of solvent evaporation, microphase separation and the processes which contribute to film hardening (i.e., viscosity, inorganic condensation) can be summarised in a simple rule: winning the "race towards order" results in a better organisation. Whenever possible, an initial system has to be designed to be flexible, in order to permit rearrangements that will lead to highly ordered systems upon post-synthesis treatment.

The organic functions incorporated impart tuneable properties in a variety of aspects: refraction index, wetting, mechanical properties, selective molecule trapping, controlled liberation and creation of reactive nanocavities, to mention but a few. Film processing adds further possibilities, such as connection to electrodes or electronic circuits, or other applications such as photo- or magnetoactivation, among others. The precise tailoring of the number, type and location of organic functions within the pore opens great possibilities to achieve highly controlled reactive systems, mimicking enzymes or biological systems. Multifunctional molecules can be designed to control the disposition and distance between functions.[94] No doubt, MHTFs are gaining enough momentum to be considered a field on its own in the near future.

However, there are some issues that need to be clarified, particularly in the refined characterisation and in the evaluation of properties, such as the detailed location of the organic functions within the pore, the pore accessibility or the effects of pore functionalisation on transport properties and selectivity towards guest molecules. The use of electrochemical methods,[95] or the incorporation of molecular correlation tools, such as 2D FTIR[53] or optical probes,[96] should expand this frontier.

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