CHAPTER XI

Hybrid Mesostructured Thin Films.

Introduction

Hybrid mesostructured thin films could be classified into two general classes following the nature of the interaction existing between the organic and inorganic parts. Class I corresponds to hybrid systems in which organic compounds (molecules, oligomers or low molecular weight organic polymers) are simply embedded in inorganic matrices. On the contrary, class II corresponds to hybrid organic-inorganic in which organic and inorganic components where both bonded through stronger covalent or iono-covalent chemical bonds. It is worth mentioning that doped-materials (Class I) involve most of the time a host-guest relationship with included species whereas the functionalize ones (Class II) imply a deeper relation since supplementary organic compounds participate more actively to the materials.

I. Doped Hybrid Mesoporous Thin Films and Nanocomposites: Class I

1. Dyes incorporation and fluorescence-based investigations

In the literature, examples of doped mesostructured hybrid films (Class I) are scarce compared to grafted ones (Class II). Historically, they result from in situ or steady-state investigations with fluorescent dyes on local environments provided by as-synthesized thin films, i.e. before removal of template. These studies are based on specific spectroscopic responses (fluorescence depolarization, solvent-sensitive emission band, lifetime, excimer/monomer emission) of fluorescent dyes towards polarity, rigidity/microviscosity of their direct environment. Briefly, it was shown that hydrophobic dyes are incorporated in the hydrophobic part of micelles. These dyes do or do not interact with the polar head groups of surfactant. On the other hand hydrophilic dyes are incorporated in the silica framework and inside the ionic interface composed of water and polar head groups of surfactants. The specific localization of dyes in thin films was used to study the energy transfer occurring between 2 dyes located in the organic part. It is noteworthy that even if these investigations involved low amount of probes usually, a high loading was reached (up to 1 pyrene for 5 CTAB that is to say 0.05 pyrene for 1 TMOS) without dye aggregation and without loss of mesostructure order.

These studies revealed that the mobility of dyes inside thin films are usually restricted especially when compared to free micelles in solution but increases with temperature. This loss of mobility was assigned to the confined state of micelles in mesostructured thin films. However, it has been demonstrated recently that a single dye could explore the mesostructure over a wide range in a relatively short time (up to several micrometers in 500 seconds). This mobility also appears to depend on the phase present in the pores since dye motion is observed for as-synthesized thin films and calcined films rehydrated under high humidity conditions on the contrary to dry calcined films. This difference of mobility between all these studies cited above is most probably due to the difference of observation time-scale (much longer for the last three ones) and to the difference of diffusion rate of the mesophase considered (diffusion is much faster in a 2D-hexagonal phase compared with the most often studied: a lamellar phase).

Another approach to mesostructured thin films of class I consists in incorporating dye molecules in calcined silica/titania mesoporous thin films. These films are synthesized via a simple immersion of films inside dye containing solutions. In order to increase the loading and in some extent to limit leaching of the dyes, aluminosilica thin films were also tested. These latter thin films showed a better adsorption ability towards a cationic photochromic dye than pure silica ones due to specific anionic sites provided by the incorporation of aluminum in the inorganic network. In addition, the concentration of the dye in thin films was higher than in solutions whatever the solvent considered and without aggregation. Finally, after dye absorption in these films, the chromophore mobility is high enough to perform photoisomerization reactions.

2. Host matrices for carbon nanotubes synthesis

Besides optical properties that mesostructured thin films could exhibit after dyes doping, these materials were successfully used as host matrices to elaborate new hybrid nanocomposites. In this case, mesoporous thin films serve as nano-reactors for chemical reactions. The simplest reaction was the synthesis of rare earth ion complexes in the same time that mesostructuration occurs.

They were also used as efficient template to synthesize carbon nanotubes. The synthesis of carbon nanotubes involves 3 steps. It implies first the synthesis of mesoporous thin films followed by a calcination step.
Thin films were deposited onto conductive substrates as indium-tin oxide glass (ITO) or gold layer. Once the surfactant was removed, a small amount of metal as catalyst (Co\textsuperscript{18} or Fe\textsuperscript{19}) was electrodeposited into the bottom of the pores of mesoporous thin films. Metal precursors could also be incorporated in the starting sol and reduced in a H\textsubscript{2}/N\textsubscript{2} flow after a calcination step.\textsuperscript{20} Then carbon nanotubes were synthesized at high temperatures (700~750\degree C) via catalytic decomposition of alcohol vapor\textsuperscript{18} or acetylene gas.\textsuperscript{19,20} It is noteworthy that this procedure implies to work preferentially with a three dimensional mesophase (here, I\textsubscript{m\textsuperscript{3}m} or I\textsubscript{a\textsuperscript{3}d}) since the 2D-hexagonal phase is more fragile and tends to collapse,\textsuperscript{21,22} and molecular transport from the top to the bottom of thin films is favored with 3D mesophase.\textsuperscript{22} Following this synthesis procedure, the highly aligned carbon nanotubes arrays grew from the bottom to the top of pores with a very uniform diameter corresponding to the pore diameter and hollow open ends. As carbon nanotubes are hollow with open ends, it is also possible to fill them with metal by electrodeposition reaction leading to metal nanowires (here Fe) encapsulated in carbon nanotubes.\textsuperscript{19}

### I.3. Hybrid polymers-POMTFs nanocomposites

The same approach was used to elaborate other hybrid nanocomposites with growth of polymers (polyethylene) inside the pores.\textsuperscript{23} After deposition and calcination steps, the mesoporous thin films were immersed in solutions containing the catalysts: dicyclopentadienyltitanium dichloride and methylalumoxane. The polymerization took place via addition of ethylene monomers in gas phase at room temperature.

A simpler and efficient alternative to synthesize hybrid polymer-mesoporous thin films was done by Coakley \textit{et al.}\textsuperscript{24} and Jang \textit{et al.}\textsuperscript{25} Here, polymers were spin coated on the top of calcined mesoporous titania thin film. An adapted heat treatment (above glass-transition temperature, \textit{T}_g) allowed the infiltration of polymers inside the pores. The authors\textsuperscript{24} demonstrated that polymers fully penetrated inside the mesoporosity from the top to the bottom of thin films. They suggested that the conformational entropy loss of polymer due to its confinement in pores was compensated by a strong enthalpic interaction between the highly polarizable chains of the polymer and the polar titania surface. In fact, they proposed that a chain of the polymer could infiltrate the mesoporosity only if some of its segments are able to absorb on the walls of titania surface. Once inside thin films, the polymer chains presented a different conformation compared to neat films of polymers: in mesoporous thin films, they are coiled and unable to \pi-stack.

The last way reported\textsuperscript{26,27} is undoubtedly the most elegant one and consists of a “one-pot” synthesis, \textit{i.e.} all the components of thin films (surfactant, inorganic precursors, solvents, catalysts, monomers) are mixed together in the same starting sol.

The first attempt was to use polymerizable amphiphilic diacetylene molecules as both structure-directing agents and monomers.\textsuperscript{27} By tailoring the size of the oligo-(ethylene glycol) headgroup of the diacetylene-containing surfactant, they synthesized conjugated polymer/silica nanocomposites with hexagonal, cubic, or lamellar mesophases. The polymerization of diacetylene units initiated by ultraviolet light converted the colorless mesophase into a blue polydiacetylene-silica nanocomposite.

The second attempt is more conventional since surfactants and monomers are distinct compounds\textsuperscript{26} (this approach was also used to form class II polymer nanocomposite thin films via introduction of a sylilated coupling agent in the starting sol\textsuperscript{28-30}). In this case, two monomers were used: 2,5-diodothiophene and acetylene. The first one was solubilized in the starting sol with a catalytic complex and the second one was incorporated in gas phase with triethylamine at room temperature under pressure. This procedure lead to a cubic mesostructured conjugated poly(2,5-thienylen ethynylen)/silica nanocomposites.

### I.4. Living cells encapsulation

All the literature cited above involves organic molecules or polymers as organic part of hybrid materials. Recently, Baca \textit{et al.}\textsuperscript{31} immobilized successfully living cells in mesostructured thin films. However the encapsulation of living organisms in matrices requires overcoming serious difficulties as cell viability throughout the synthesis process. It implies for example biocompatible surfactants. Indeed surfactants used in templated mesoporous silicas are detergent monomers that insert into cell membranes and lead to their solubilization, inducing rapid cell death. Thus, standard surfactants were replaced by phospholipids, which are integral components of the cell membrane. The choice of phospholipids species must be done in respect of 3 parameters: they should (i) present minimal disruptive electrostatic interactions with cell membranes, (ii) be soluble in water and (iii) have sufficiently small critical packing parameters \textit{g}\textsuperscript{22} to direct the formation of high curvature 3D (hexagonal or cubic) lipid-silica mesophases.

However, even if diacylphosphatidylcholines were identified as suitable template, the incorporation of living cells markedly altered the mesostructuration process in several ways. During EISA process, cells rapidly organized around themselves a lipid-rich shell excluding largely silica. Moreover, the living cell \textit{S. cerevisiae}
globally altered the sequence of mesophase development during EISA process leading to a 2D hexagonal mesophase instead of a 3D hexagonal/cubic one. On the contrary to conventional organic moieties, living cells are dynamic structures able to sense and response to their environment. As solvent evaporates, the concentration of osmolytes in the system increases. Stationary-phase cells can release up to 35% of their cellular water volume in response to a change in turgor pressure in the cell membrane, which would increase the volume of water in the surrounding lipid shell by more than 60%. The resulting pH gradient that develops around the cell in turn affects both the local lipid interface and the host lipid/silica matrix. This pH gradient favors both conversion of lipid bilayers into ordered lamellar mesophase (instead of the 3D hexagonal/cubic phase expected) and enhancement of silica condensation around cells hindering diffusion of silica oligomers.

Despite all the potential applications described above of doped-mesostructured thin films (Class I), the localization of the organic components in the micellar part or/and the opened pores of mesostructured thin films could limit their potential applications mainly due to the high tendency of organic molecule leaching. Then it is most of the time necessary to graft organic molecules via covalent or iono-covalent bonds to the matrix.

II. Functionalized Hybrid Mesoporous Thin Films: Class II

II.1. Grafting Routes

Two grafting routes are commonly used to incorporate organic functionalities into POMTFs: the “one-pot” synthesis and the post-funtionalization (see the accompanying figure). The first one, i.e. “one-pot” synthesis, involves a co-condensation step between a functional inorganic precursor, generally an organosilane, with an inorganic precursor (typically TEOS or TMOS and less frequently Transition Metal Oxides) in the presence of templates. In this case the mesostructuration process and functionalization take place at the same time. In the second one, i.e. post-functionalization, chemical modifications come off once mesostructuration and calcination steps are achieved, via solution impregnation or vapour treatment through chemical bonds with silanol or M-OH groups covering the pore surface. The “one-pot” synthesis was largely dedicated to functionalize silica POMTFs while post-functionalization was used with silica and TMOs matrices. However, the “one-pot” synthesis of transition metal oxide has been recently reported either via the use of organosilane precursors or with a complexing/chelating agent. In this latter case, the complexing/chelating agent, trifluoroacetic acid, was randomly distributed within the inorganic framework and was rather used to control the rate of titania condensation.
Despite the fact that post-functionalization was widely exploited to modify properties of mesoporous powders (for an overview on functionalization of mesoporous powders, see the following reviews 37,38), the most frequent route leading to functional POMTFs is the “one-pot” synthesis. In fact, this approach allowed to synthesize POMTFs bearing a vast choice of organic functions (for a more detailed description of functional groups incorporated into POMTFs, see the following review 39). These functional groups could be chemically inert as for example alkyl chains,40-43 or aromatic groups,43 but also more reactive as aminoalkyle,33,43-46 methacryloxypropyl,29,43 etc … or presenting intrinsic properties as silylated dyes45,46,49 which could serve as sensors4,6,50-53 or more sophisticated materials as nanovalves.34 The co-condensation route generally leads to a more homogeneous distribution of organic functionalities into mesoporous matrices with a high control of the stoichiometry. The final materials exhibit a small decrease of the pore sizes and pore volume only. However, the synthesis could be more delicate due to different effects of organic functions on mesostructuration process of POMTFs.39,55 The influence of organic functions generally limits the organic/metal molar ratio which is often restricted to 20 %. However, higher loadings of organosilanes in POMTFs, from 50 to 100%, were achieved either by a careful control of hydrolysis - condensation steps56-58 or by using hybrid bridged silsesquioxanes59,60 and methyl-triethoxysilane.41,61

On the other hand, post-functionalization overcomes some difficulties related to the “one-pot” synthesis. Since mesostructuration process and grafting are two distincts steps, the influence of organic functionalities is seriously restricted. Moreover, the thermal treatment at high temperature (> 500°C) allowed by the absence of organic functionalities favors more stable matrices. However, this method often leads to a quite low loading, an inhomogeneous distribution of the functional groups inside matrices, a decrease of the pore volume and even, in extreme cases, a complete closure of the pores.38 Moreover, depending on the post-grafting conditions (impregnation), the inorganic network could be partially damaged due to capillary stresses or chemical cleavage of M-O-M bonds. Recently, another alternative route, vapour infiltration treatment, was successfully tested without reducing the pore size and with an increase of mechanical strength. Briefly, neat surfactant mesophases62 or as-synthesized silica thin films52,63,64 were first coated on a substrate and a subsequent organosilane or hexamethyldisilazene vapor treatment was then applied leading to functionalized POMTFs. This subsequent vapour treatment has been also realized on calcined POMTFs.65 A similar method has been developed recently using supercritical carbon dioxide as synthesis medium.66 In table 1 are reported the advantages and drawbacks of both methods.55

Although the vast majority of functionalized mesostructured thin films are obtained via “one-pot” and post-functionalization pathways, combined routes have been investigated. This combined approach could occur when organosilanes are not commercially available. Instead of synthesizing the desired organosilanes before film synthesis, some authors elaborated hybrid thin films through co-condensation or post-functionalization procedure with an organosilane bearing a reactive function (typically amino,46,67 thiol,68 isocyanato,69 iodo67 groups). After removal of surfactant, the post-modification involving the reactive function anchored into thin films and the organic molecule (fluorescein derivative,66 ferrocenecarboxylic acid,67 azobenzene derivatives,69 β-cyclodextrin69) could take place. This combined approach presents the advantages both to avoid the synthesis of a too intricate organosilanes and to limit the influence of organosilanes (often bulky) on mesostructuration process.

Table 1. “One-pot” synthesis versus post-functionalization.55

<table>
<thead>
<tr>
<th>“One-pot” synthesis</th>
<th>Post-functionalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailor compatibility R-MXₙ and MXₙ</td>
<td>Tailor surface-R-MXₙ interactions and reactivity</td>
</tr>
<tr>
<td>Network consolidation temperature limited by the thermal stability of organic groups</td>
<td>High pre-condensation temperature (calcination step possible) before grafting, leading to a more stable inorganic network</td>
</tr>
<tr>
<td>Localization of organic groups in the pores and/or embedded in the framework depending on the nature of the organic groups</td>
<td>Organic groups grafted mostly on pore surface</td>
</tr>
<tr>
<td>Organic groups have a role in the mesostructuration process (e.g., polarity, condensation catalysis, cosurfactant etc…)</td>
<td>Mesostructure is determined before organic group incorporation</td>
</tr>
<tr>
<td>Relatively homogeneous dispersion of organic groups</td>
<td>Pore blocking possible</td>
</tr>
<tr>
<td>Limited by chemical compatibility</td>
<td>Limited by diffusion plus pore blocking</td>
</tr>
<tr>
<td>One-pot synthesis, one or more functions, lower control of dispersion</td>
<td>One post-graft, one function, successive possible</td>
</tr>
</tbody>
</table>

Table 1. “One-pot” synthesis versus post-functionalization.55
II.2. Co-condensation or “one-pot” synthesis

The “one-pot” synthesis has been used to synthesize almost exclusively hybrid silica-based mesostructured thin film via co-condensation of organosilanes with TEOS or TMOS. However, Soler-Illia et al.\textsuperscript{33,34} reported recently the one-pot synthesis of highly ordered hybrid mesoporous thin films \((M_{1-x}(SiR)xO_2)\) obtained by co-condensation of organotrialkoxysilanes \((R-Si(OE)_3)\) with \(R = \) propylamine, propylthiol and phenyl with transition metal chloride \((MCl_4 \text{ with } M = \text{Zr or Ti})\). Such mixed oxide hybrid matrices allow a further selective functionalization with metal chelating agent leading to bifunctional materials. Bifunctionalization could also be achieved with pure silica matrices by a one step procedure.\textsuperscript{11,60,70}

Data concerning one-pot synthesis of mesoporous thin films are gathered in table 2. The non commercial available organosilanes, the surfactant and experimental conditions, the nature of the mesophase, the targeted applications and the authors are reported.

<table>
<thead>
<tr>
<th>Functional organosilanes</th>
<th>Properties / applications (ref)</th>
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<th>Properties / applications (ref)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Triethoxydibenzoylmethane</td>
<td>Heavy metals sensor\textsuperscript{51} BF3 sensor\textsuperscript{51}</td>
<td>8) Silanized Eu(III) phenantroline</td>
<td>Nonlinear optical materials, tunable solid-state lasers\textsuperscript{51}</td>
</tr>
<tr>
<td>2) Dye-NH(CH\textsubscript{2})\textsubscript{3}-Si(OCH\textsubscript{3})\textsubscript{3} Dye = 5,6-carboxyfluorecein, succinimidyl ester (5,6-FAM, SE)</td>
<td>pH sensitive\textsuperscript{56}</td>
<td>9) Eu(III) bis(N,N'-phenyl 3-triethoxyisilylpropyl)-2,6 pyridine dicarboxamide</td>
<td>Fluorescent probe\textsuperscript{11,13}</td>
</tr>
<tr>
<td>3) 4-(3-triethoxysilylpropyl ureido) azobenzene</td>
<td>Smart gas masks, membranes, controlled release systems, externally controlled micro/nanofluidic-channel systems\textsuperscript{54}</td>
<td>10) Tb(III) N,N'-bis-(3-triethoxyisilylpropyl)-2,6 pyridine dicarboxamide</td>
<td>Fluorescent probe\textsuperscript{11,13}</td>
</tr>
<tr>
<td>4) Ru(II) 2,2'-bipyridine-2-aminoethyl-2-aminopropyl –trimethoxysilane</td>
<td>Fluorescent probe\textsuperscript{11,73}</td>
<td>11) N-[(3-triethoxysilyl)propyl]-2carbomethoxyfulleropyrroliidine</td>
<td>Optically encoded information storage for read only materials (ROMs)\textsuperscript{\textsuperscript{54}}</td>
</tr>
</tbody>
</table>
Although the one-pot synthesis presents several advantages compared to post-grafting, this approach is somehow complicated and several difficulties exist in addition to the control of the main parameters related to the EISA process. For example, the presence of organosilanes presenting different reaction rates and self-assembly can modify or even hinder mesostructuration. Moreover, an increasing proportion of organosilanes in the reaction mixture favors homocondensation reactions to the detriment of cross-linking co-condensation reactions with the silica precursors leading to an inhomogeneous distribution of different organic functionalities in the framework. In addition to that the temperature of the network consolidation step should be adapted to the organic compounds present inside the matrices. In the following sections, an overview of the main difficulties reported by the literature will be developed.

II.2.1. Chemical and Processing Parameters (EISA parameters)

The EISA method, which is used in almost all the syntheses of functionalized and mesostructured silica thin films, implies a homogeneous starting sol. However, when the silylated probe is poorly soluble or insoluble in the alcoholic sol, segregation or aggregation can take place. This phenomenon may be due to an insufficient hydrolysis rate of the organosilane precursor, resulting in hydrophobic species. In some cases, the precursor can be insoluble regardless of the hydrolysis time. To overcome these problems, a pre-hydrolysis step of the organosilane in a weak acidic medium \(^7\) and/or the use of a cosolvent are required.

The choice of cosolvents is limited: the cosolvent must not only dissolve the desired organofunctional molecule but also be miscible with the starting sol without causing organosilane gelation and affecting neither the film optical quality nor the mesostructuration. Moreover, the cosolvent must present evaporation ability close to that of ethanol and assure a good wettability towards coating substrates. In addition to that the amount of cosolvent in the initial sol should be adapted to avoid phase separation during evaporation process (higher than the quantity needed to solubilize the organosilane especially when its boiling point is lower than ethanol). The cosolvent most commonly employed in the literature is the tetrahydrofuran. This cosolvent, used in place of ethanol or in a mixture with ethanol, has been successfully employed for preparing well-organised thin films with monomers, \(^{27,28}\) \(\beta\)-diketones, \(^{31}\) C\(_{60}\) and quinizarine derivatives, \(^{42,75}\) bridged silsesquioxane \(^{81}\) or with MTES-based matrices. \(^{41}\)
The presence of organosilanes could also modify the hydrolysis – condensation rates of silica species. For example, organosilanes bearing a basic function, typically an amino group, catalyze hydrolysis and condensation reactions of the silica precursor and can yield the fast gelation of the sol. Acidic conditions in EISA are important to make films which present good (optical) quality, which is a very important feature for applications in optics and optical sensors. In order to avoid basic catalysis of silica species, amino groups are first usually neutralized with a strong acid prior to the addition of the silica precursor. A subsequent treatment of the films with ammonia could allow the recovery of the amino group through deprotonation of the ammonium. However, gelation process could not be always hindered. For example, high loading of ruthenium complexes in the initial sol leads to gel formation. On the other hand, the presence of methyltriethoxysilane in hybrid MTES-TEOS thin films or vinyltriethoxysilane with TMOS slows down the polycondensation of silica. This is beneficial since hybrid MTES-TEOS mesostructured thin films are highly ordered and defect-free.

A recent approach leading to well-ordered hybrid POMTFs with a high content of organosilanes has been developed. A majority of hybrid POMTFs results of one step co-condensation, i.e. organosilanes and inorganic precursors (TEOS/TMOS) are mixed in the same time in the initial sol, but this one step co-condensation gives usually poorly organized hybrid POMTFs at high loading of organosilanes. Some authors reported an alternative “one-pot” synthesis highlighted by Matheron et al. This synthesis is based on a pre hydrolysis-condensation step of TEOS followed by the addition of organosilanes just prior the sol deposition. These conditions limit considerably the condensation of organosilanes before film deposition and consequently do not disrupt significantly the mesostructuration process.

This “delayed” synthesis modifies the main EISA parameters as surfactant/inorganic precursor molar ratio and the optimum relative humidity within the dip-coater. It was observed that the CTAB-TEOS mesophase diagram was shifted towards higher CTAB/TEOS ratio and that this shift increased with the organosilane content. Typically, a 3D-hex mesophase obtained for a CTAB/TEOS ratio of 0.08 with pure TEOS is shifted to 0.16 for 20 % of MTES (MTES/TEOS ratio = 1/4) and to 0.20 for 50 % (MTES/TEOS ratio = 1/1). In the same time, the increase of MTES content in thin films (from 0 to 50%) causes a decrease of the optimum relative humidity (RH) value (from 65 to 40% in the case of a 3D-hexagonal mesophase). These changes of optimum RH values were explained by the necessity to obtain rapid gelation of the deposited sol in order to stabilize 3D mesophases (3D-hexagonal and 3D-cubic) which do not exist in the phase diagram of CTAB with water and ethanol. This “delayed” procedure allowed to synthesis well-organized hybrid POMTFs with high content of methyltriethoxysilane-MTES (50%), vinyltriethoxysilane-VTES (30%) and trifluoropropyltrimethoxysilane-TFPTES (20%).

II.2.2. Localization of Grafting Compounds

In order to control the final properties of functional thin films, it is of great importance to localize perfectly organosilane species in the mesostructure and to address a specific compound to a specific place. The localization of such species inside the mesophase has been investigated either directly by spectroscopic techniques such as fluorescence, UV-visible absorption and micro-Raman spectroscopies and/or indirectly by studying structural changes induced by the incorporation of probes (e.g. variation of the lattice parameters, phase transition, formation of mesophase at very low surfactant/TEOS ratio). With regards to mesostructured thin films made with ionic surfactants such as CTAB, the structure can be divided into 3 main regions, the silica framework, the ionic interface formed by the charged surfactant heads, the hydroxysilated silica surface and the organic region composed by the hydrophobic core of the micelles. This organic/inorganic phase separation is also obtained with non ionic surfactants such as triblock copolymers (i.e. poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) PEO – PPO – PEO)-based thin films. However, in this case, the limits between the three phases, silica wall, hydrophobic PPO block and hydrophilic PEO block, are less defined mainly because of interpenetration of the PEO and silica networks.
According to the literature, the silylated functions can be classified into two categories (see the figure below):

- Monosilylated compounds, F-Si(OR)$_3$, constituting the most common category studied (with –OR condensable groups, F the functionality and S the spacing group)
- Multisilylated probes of general formula: F(Si(OR)$_3$)$_n$, mainly composed by Si(OR)$_3$-F-Si(OR)$_3$ bridged silsesquioxanes and rare earth complexes with silylated organic ligands

The localization of organosilanes is governed by their physico-chemical properties. Several factors have to be taken into account such as the hydrophilic/hydrophobic balance of the organosilane molecule, the number of anchoring functions (–OR)$_3$, the length and the nature of the spacing group (group S between the functionality F and the anchoring function –Si(OR)$_3$), the nature of the functionality F (hydrophobic, hydrophilic, ionic, polar, apolar, aromatic for example).

A general tendency is commonly observed with probes presenting multiple trialkoxysilane functionalities. They are mainly incorporated inside the inorganic network, as was observed with multisilylated rare earth complexes$^{11,72,73,77}$ or even compose the walls of the framework as observed with hybrid bridged silsesquioxanes$^{59,60,66}$ (and also the monosilylated methyl-triethoxysilane$^{41,61}$) leading to mesostructured thin films with concentrations as high as 100 % in organosilanes.

However, most of the common organosilanes are monosilylated with a general formula F-Si(OR)$_3$. Such molecules possess two different groups, one carrying the functionality and the other being the condensable groups. Both groups simultaneously interact with two different regions of the mesostructure. The condensable –OR groups allow the formation of chemical bonds between the molecule and the framework. It is interesting to point out at this stage that even if most studies reported in the literature concern pure silica frameworks, the use of such compounds is also compatible with organosilica frameworks (bridged bistrialkoxysilanes$^{60}$; or surprisingly, with transition metal oxides like ZrO$_2$ or TiO$_2$.$^{33,34}$ The localization of the functionality F is mainly governed by the “philicity” concept (or “like” dissolves “like”) but also by specific interactions such as cation–π$^{85}$ or ionic.$^{11}$

Generally, the solubilization of lipophilic molecules occurs in the hydrophobic micelle core and the placement of hydrophilic molecules either in the ionic interface or in the framework. For example, Nicole et al.$^{51}$ investigated the incorporation of a hydrophobic chelating agent in thin films: a silylated β-diketone. β-diketones are well known to exist mainly in two tautomeric forms in equilibrium. As the keto-enol equilibrium is extremely solvent-sensitive and as the ketone and enol forms present two distinct UV-visible spectra, it was
possible to determine spectroscopically the placement of the silylated β-diketone in thin films. Indeed, the absorption spectra of the β-diketone in thin films, whatever the mesophase studied (Pm3n, p6m, lamellar), have the same aspect that of the probe dissolved in THF, indicating that β-diketone environment is apolar, suggesting their localization inside the hydrophobic core of the micelles (see the figure below).

On the other hand, Zink et al.11,73 observed that the localization of a silylated ruthenium complex positively charged depended on the surfactant charge. In SDS (anionic surfactant) based thin films, the ionic complex resided in the ionic region at the interface between the organic and inorganic regions, while, in mesostructured thin films made with cationic surfactant (i.e. CTAB), the complex was located in the silica network. These results suggest that the electrostatic repulsion between the positively charged Ru complex and cationic CTAB headgroups makes the ionic region less hospitable than the silicate matrix, thus forcing the Ru complex to enter into the silicate matrix.

Cagnol et al.43 noticed that the structure of the final mesophase depended on the loading rate of (2-phenylethyl)trimethoxysilane in thin films. For low amounts of organosilanes, the mesostructure was not modified, presenting a cubic structure (Pm3n), whereas for high amounts of probe, a 2D-hexagonal (p6m) phase was formed (see the following figure).
Such phase transitions are commonly observed when the [CTAB]/[SiO₂] ratio increases,⁸⁶ inducing a decrease in the curvature of the micelles. It is generally agreed that two kinds of sites are available when a molecule is solubilized inside micelles: one near the polar head and the other between alkyl chains in the hydrophobic core of the micelles.⁸⁷ It has been shown⁸⁸ that the first sites occupied by aromatic compounds is near the polar head of CTAB surfactants due to specific interaction between the π system and the quaternary ammonium.⁸⁵,⁸⁹ Once the first sites are saturated, the solubilization occurs in the hydrophobic part of the micelles, inducing a decrease of the curvature of the micelles and causing a phase transition. However, the length and the nature of the spacing group, S, could hinder the natural placement of hydrophobic functionality inside the micelles. For instance, with the same functionality (i.e. phenyl group) and the same relative amount of probes, no variation of mesophases was observed with the phenyltriethoxysilane, on the contrary to the (2-phenylethyl)trimethoxysilane.⁴³ This result could be explained by a physical impossibility of the aromatic functionality to fully reach the hydrophobic part of the micelles in the case of the phenylethyl-based precursor, thus “preventing” the swelling of the micelles and the decrease of the interface curvature (see the figure below). This geometrical criterion is in balance with all other parameters described previously.

Consequently, the role of the organic function during the self-assembly is complex, mainly because the key parameter leading to a particular mesophase is not always predictable. The functionality and the spacing group may interact with the silica wall, with the surfactant head group, and with its hydrocarbon tail, affecting in some case the curvature of the hybrid interface.

II.2.3. Mesostructures Modifications

We have seen previously that spectroscopic techniques (i.e. absorption, UV-visible or fluorescence spectroscopies) are a useful tool to determine the placement of organosilanes inside mesostructured thin films. Nevertheless, the incorporation of such compounds inside thin films could also cause structural changes, from variations of the lattice parameters to phase transitions and even allows the formation of a mesophase for a (very low) molar ratio surfactant/silica leading to an amorphous thin film without organosilanes. All these changes give an indirect proof of the localization of the organosilane inside mesoporous thin films.

The changes of the lattice parameters with an increasing amount of organosilane could be an indication of its preferential localization at the ionic interface, near polar heads of the micelles.⁴³ In the system CTAB-TEOS, the incorporation of a positively charged organosilane, 2-(trimethoxysilyethyl)pyridinium, induced the formation of a 2D-hexagonal phase (p6m), regardless of the loading ratio.⁴⁵ The authors observed a progressive increase of the intertecticular distances d(01) with the increasing incorporation of protonated ammonium...
functions. This observation also occurred with the two other positively charged groups studied (i.e. 3-(2,4-dinitrophenylamino)propyltriethoxysilane and 3-aminopropyltriethoxysilane). These results could be primarily attributed to the cationic character of the incorporated functions. Usually, in acidic conditions, the bromide is intercalated between the ammonium head group and the silica wall through electrostatic interactions.\textsuperscript{90} In this case, the electrostatic repulsion between the two positively charged groups (i.e. the polar head of the surfactant and the functionality, $F$, of the organosilane) governs the formation of the mesophase with a main localization of the probe in the ionic interface, even if a swelling effect could be involved (see the figure below). These results are in agreement with the spectroscopic study of the group of Zink concerning the localization of a positively charged silylated ruthenium complex in CTAB-based mesoporous silica thin films.\textsuperscript{11}

![Diagram showing the effect of probe incorporation on mesophase formation](image)

The incorporation of probes could also lead progressively to a destructuration of the mesophase with few changes in the lattice parameters, as in the case of 3-cyanopropyltriethoxysilane from a well ordered 2D-hexagonal structure to a vermicular phase.\textsuperscript{48} This modification could be explained by a solubilization of the cyanopropyl groups inside the surfactant micelles. Another example of phase transitions was reported with the incorporation of bulky hydrophobic compounds.\textsuperscript{51,75} The addition of increasing amounts of dibenzoylmethane/quinizarine derivatives for a fixed CTAB / silica molar ratio induces mesostructural evolutions in thin films. The following sequence was observed: cubic phase (Pm\textsubscript{3}n) $<$ mixture of cubic (Pm\textsubscript{3}n) and 2D-hexagonal (p\textsubscript{6}m) $<$ pure 2D-hexagonal phase $<$ lamellar phase (see the following figure). Such phase transitions are explained in terms of variation in the packing parameter $g$. The increase of the packing parameter can be due to solubilization of large species preferentially in the hydrophobic part of micelles during evaporation of solvents, leading to an increase of the total volume associated to the surfactant chain. This mechanism is supported by the UV-visible experiments performed on hybrid thin films.\textsuperscript{51,75} In this case, the incorporation of large species causes direct phase transitions without modifications of the lattice parameters.

![Diagram showing phase transitions](image)
This co-solvent effect allows the formation of a mesophase for conditions at which mesostructured thin films are not usually obtained (i.e., very low surfactant on silica ratio). The synthesis of mesoporous thin films with 10% mol. of perfluoroalkylsilanes with long chains, typically tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxysilane and heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane, have been achieved with sol containing a ratio CTACl/Si ~ 0.004. It is interesting to point out, following the phase diagram of CTAB/Si/H₂O ternary system, that the lowest ratio CTAB/Si leading to the formation of mesostructured thin films is equal to 0.10. Moreover for this last ratio, we could expect only a 3D-hexagonal mesophase (P₆₃/mmc), which is a structure with a higher curvature of the micellar interface than the 2D-hexagonal phase (p₆m) observed with the addition of the perfluoroalkylsilanes. This result suggested that perfluoroalkylsilanes also act as a structure-directing agent when the reactant was mixed with a small amount of surfactant. Indeed, hydrolyzed perfluoroalkylsilanes carrying hydrophilic silanol head groups and long hydrophobic perfluoroalkyl chains can be clearly amphiphilic molecules.

We have seen that the function, F, could develop direct interactions with surfactant-head groups. These interactions increase the area of the surfactant’s head group, promoting higher curvature of the micelles promoting Pm₃n structure. The opposite effect on the curvature would be obtained by increasing the volume of the hydrophobic micelle core (swelling effect). However, in a particular system, one has to keep in mind that the effect of each function is more subtle and cannot be sketched by only these two extreme effects.

II.3. Post-functionalization Route

The other route leading to hybrid POMTFs consists of post-grafting organic functions onto stabilized inorganic network. The difference of reactivity between silica and TMOs implies to distinguish these two matrices towards post-functionalization. Indeed, grafting on silica matrices involves covalent bonds due to condensation reactions with organosilanes species which are also able to react on themselves. On the contrary, TMOs matrices are functionalized via iono-covalent bonds with complexing/chelating agents which can only react with inorganic matrices. Moreover, the strength of bonds, from iono-covalent to covalent, could influence dramatically the properties of the resulting hybrid matrices in terms of diffusion, accessibility, homogeneity. The grafting of silica could be considered as irreversible while functionalization of TMOs is based on complexation equilibria. Such differences render silica matrices much more sensitive to pore blocking due to extensive condensation of silica species. This problem has been limited by new post-functionalization treatments: vapor infiltrations of organosilanes or hexamethyldisilazane on as-synthesized POMTFs.

From this short overview, it appears that two main parameters are of great importance for obtaining a homogeneous distribution of organic functions in POMTFs: (i) the accessibility of the porosity (large diffusion of molecules inside the whole film) and (ii) the reactivity of the molecules towards matrices and among themselves. The diffusion properties essentially depend on the mesophase (two-dimensional or three-dimensional), the pore interconnection (presence of restrictions or no interconnection for example), the pore size and the pore morphology (spherical, cylindrical, ellipsoidal for instance).
Post-functionalization could also be used to elaborate bifunctional POMTFs. Briefly, in the first step, a hybrid M-(RSi)O₂ POMTF (M=Ti, Zr etc.) is created by one pot co-condensation of MCl₄ and RSi-(OEt)₃. 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 transition metal sites (Ti, Zr etc.), which are freely accessible. This approach allows then both a good homogeneity of the first function (organosilane species) due to “one-pot” synthesis and a high dispersion of the second function (complexing/chelating molecules) due to the properties of post-functionalization with TMOs.

II.3.1. Post-grafting on Transition Metal Oxide Matrices

Examples of non-silica functionalized mesoporous materials are scarce, even if methods for the synthesis of transition metal oxide films have been developed, either for MO₂ / M₂O₃ or mixed oxide frameworks by a general evaporation-induced self-assembly (EISA) procedure. The feasibility of incorporating organic molecules within mesoporous zirconia thin films by post-synthesis grafting was demonstrated by Crepaldi and coworkers. The production of hybrid POMTFs is often based on the post-synthesis functionalization of titania or zirconia mesostructures with organic bifunctional molecules F–G, which contain a desired F group and a suitable grafting group (G = phosphonate, phosphate, carboxylate, acetyl acetone...) capable of performing complexation of the transition metal centers. This procedure leads to highly ordered, non-silica hybrid POMTFs with organic functions at the pore surface. An important aspect of these films is that the anchoring of the organic groups can be varied, from strong and inert (phosphate, phosphonate) to relatively labile (carboxylate), leading to a great flexibility in the attachment of organic functions, which can be advantageous for several different applications (e.g. sensors, controlled release systems). However, the post-functionalization of TMO thin films is not straightforward, and particular attention has to be paid to aspects such as surface chemistry, diffusion within pores, dissolution, etc. Another important issue is the integrity of modified mesoporous transition-metal oxides under solvent flux (i.e. function leaching), due to the fact that functions are grafted via coordination or ionic-covalent bonds to the pore wall.

In these studies, mesoporous films with a 2D hexagonal or cubic mesostructures were prepared by EISA, using a triblock copolymer (Pluronic F127) or Brij-58 [C₆H₁₃(CH₂CH₂O)₂₀OH] templates. The films were thermally stabilized by several post-synthesis treatments until complete removal of the template. A typical functionalization experiment was performed by dipping calcined mesoporous film, previously rinsed with ethanol, into a continuously-stirring solution of the chosen molecule in THF, acetone, or water.

Kinetics experiments showed that molecule incorporation occurs in two steps and that over 80% of the incorporated functional groups enters the pore system within 5 min. The remaining 20% are gradually incorporated and saturation is reached between 60 and 120 min. It has been also observed that the function incorporation depended on the mesostructure: cubic 3D mesostructures (Im3m) are more accessible than their p6m̅ 2D hexagonal counterparts. This difference is attributed to the presence of pores open to the surface in the cubic phase that were absent in the p6m̅ mesostructure. 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. Shrinkage of the p6m̅ system results in tubular pores with 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).

The trends issuing from leaching experiments demonstrate that the anchoring strength follows the complexation strength of the grafting group, that is, R–O–PO₃²⁻ > dicarboxylate > carboxylate, for groups with high solubility in the leaching solvent. The transport of the grafting molecule to the inner pores of transition metal oxide POMTFs could follow a sequence of adsorption-desorption-diffusion. Hence, a higher complexation ability of the grafting group should result in slower incorporation of the organic function. The solvent also plays an important role, particularly favoring the desorption step. For example, the leaching rates of mercapto succinic acid are higher at low pH, where the acid is fully protonated, and therefore the carboxylate anchoring groups become more labile. An interesting characteristic of these hybrid POMTFs is that, contrary to the irreversible grafting observed in mesoporous hybrid silica, anchoring groups with different strengths can be selected to obtain a wide variety of responses, from strongly attached functions to functions that can be liberated by external stimuli (pH). Moreover transition metal oxides POMTFs could be also processed as multilayer stacks with silica or hybrid silica POMTFs and were selectively functionalized by complexing molecules.
II.3.2. Post-grafting on Silica-Based Matrices

As described previously, the most commonly employed method to functionalize mesostructured silica thin films is the one-pot synthesis. However, some studies employing post-functionalization have been reported either via vapour phase infiltration or via immersion in a solution. It is interesting to notice at this stage that the majority of post-functionalized silica POMTFs are devoted to (ultra)low-\(k\) materials especially those made via vapor phase infiltration.

In the post-functionalization via immersion procedure, thin films were calcined and stirred in dry toluene, ethanol or dichloromethane solution containing organotrialkoxysilane or hexadimethilsilazane species under refluxing conditions. The reaction time was varied from 4 to 24h. Finally, thin films were washed with solvent and dried at low temperature. In the alternative route, i.e. vapor infiltration, POMTFs before or after the calcination step are exposed to grafting molecule vapor in a closed vessel at moderate temperatures (150–165°C depending on the grafting molecule).

It was observed that post-grafting in some cases led to materials presenting pore restriction (bottle ink pores) or to a total blocking of the porosity. On the contrary the vapor infiltration techniques especially on as-synthesized POMTFs prevent the usual shrinkage of pores due to calcination, allow densification of walls and thus an increase of mechanical and hydrothermal stabilities of POMTFs and limit the usual reduction of pores due to grafting.

References:
