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Current Opinion in Colloid &amp; Interface Science 4 (2000) 420–427

**Current Opinion in**  
Colloid & Interface  
Science

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# Thin films of mesoporous silica: preparation and characterization

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## Abstract

Preparation of mesoporous materials in a thin film geometry was first reported in 1996. Recently, improvement of the preparation methods yielded stable films with well-defined symmetries, controlled pore orientation, continuity and film thickness. The ability to tailor film properties is important for their utilization in applications ranging from catalysis to microelectronics, where morphological control in the meso-domain is vital. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Mesoporous; Thin films; MCM

## 1. Introduction

Ordered mesoporous materials have attracted attention since their discovery by Mobil Oil Research and Development scientists in 1992 [1,2]. The class of materials with typical pore size in the range of 2–50 nm was named MCM (Mobil Composition of Matter), and each symmetry class was designated by a numerical code, e.g. hexagonal (MCM-41), bicontinuous cubic (MCM-48), lamellar (MCM-50). Mesoporous materials form when inorganic oxides (e.g. silica) polymerize in the presence of surfactants, which serve as structure directing agents for the oxide framework. Different types of surfactants, including triblock copolymers may be used as templating agents [3–7••]. Features such as structure, composition, pore diameter, pore volume and surface area can be tailored by the inorganic source material, molar composition, the template type and the condensation/hydrolysis process. The formation of the porous matrix is then followed by removal of the organic template either by

incineration at elevated temperatures ('calcination') or by liquid extraction.

The technological potential of mesoporous materials for chemical separations and heterogeneous catalysis were recognized with their discovery [8•]. A large experimental effort led to the development of a multitude of synthetic methods and a variety of templating moieties. In addition to their high applicability, mesoporous materials offer a fascinating field for the investigation of molecular behavior in confined geometries [9•].

An important feature of mesoporous materials is their ability to form thin films. While originally synthesized to yield bulk materials, methods for preparation of mesoporous materials in a thin film configuration at a thickness range of nanometers to micrometers were recently reported. The motivation for synthesis of Mesoporous Thin Films (MTF) originates from the appreciation of their technological potential as membranes [8•], sensors [10], surfaces for heterogeneous catalysis [10], and last but not least, insulating layers of low dielectric constant for microelectronics [11]. For all the above applications a thin film geometry is essential.

Mesoporous materials are rigid solids and as such

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cannot be easily shaped into thin films at the post-synthesis stage. Thus, the reactive mixture has to be deposited as a thin film, or the synthesis conditions should favor the formation of a thin interfacial layer. In the second case formation of bulk material competes with the growth of thin films. MTFs are characterized by bulk properties such as symmetry, pore diameter, surface area and stability, as well as parameters which become relevant in a thin film geometry. These include pore alignment with respect to the interfacial plane, film thickness, continuity and surface roughness. MTFs were characterized by a variety of techniques. A thorough description of the characterization techniques is beyond the scope of this review, and may be found in the literature [1,2,12–14].<sup>1</sup>

The review focuses on the description of advanced methods for preparation of MTFs. We classified the

methods according to the substrates or surfaces and their role in the preparation process. In Fig. 1 the organization of the review is presented schematically. In addition MTFs which are embedded with nanoparticles are described briefly.

## 2. Preparation of mesoporous thin films

### 2.1. Free standing mesoporous thin films

MTFs were produced at air–water [16,23,28–31•] and oil–water interfaces [32] (Fig. 1). In both cases, the films were observed to grow by the transport of material from the solution towards the interface. Films at the air–water interface were grown from a homogeneous solution of the reactants (after hydrolysis) in the water phase, while for growth of films at the oil–water interface, the water-insoluble silica source was positioned in the oil phase.

The thickness of the films formed at air–water interface ranges from tens of nanometers to several micrometers [24,30] depending on the growth period, surface-to-volume ratio of the reaction vessel, solution acidity [24] and the concentration of the silica.

Surface structure and properties of the resulting films were found to depend on the nature of the interfacial interactions. Specifically, it was observed that films grown at the air–water interface exhibit surface roughness (root mean square value, rms) in the range of 0.2 nm at the air-side, and a much larger roughness at the water side [30]. It was concluded that

<sup>1</sup>The most commonly used methods are: *Small Angle X-ray Scattering (SAXS)*, which provides quantitative structural information at length scales from 2 to 100 nm, *Gas adsorption-desorption isotherms* which measure the surface area, total pore volumes and pore size distributions [14,15•], *Transmission Electron Microscopy (TEM)*, which supplies qualitative information on the structure of the MTF, with sub-nanometer resolution both in face-on and edge-on (cross-section) projection, with an effective field of micrometers to nanometers. TEM is also useful for the investigation of the structure and level of organization of particle-filled mesoporous materials. Surface structure of MTFs at different length scales, ranging from micrometers to Angströms, can be measured by *Optical Microscopy* with micrometer resolution, and *Atomic Force Microscopy* [16–18], with nanometric resolution. *Fluorescence* [19–21], *X-Ray reflectivity* [22•,23], *acoustic wave* [21], *SEM* [15•,16,24], *FTIR* [14,25–27] are all valuable tools.

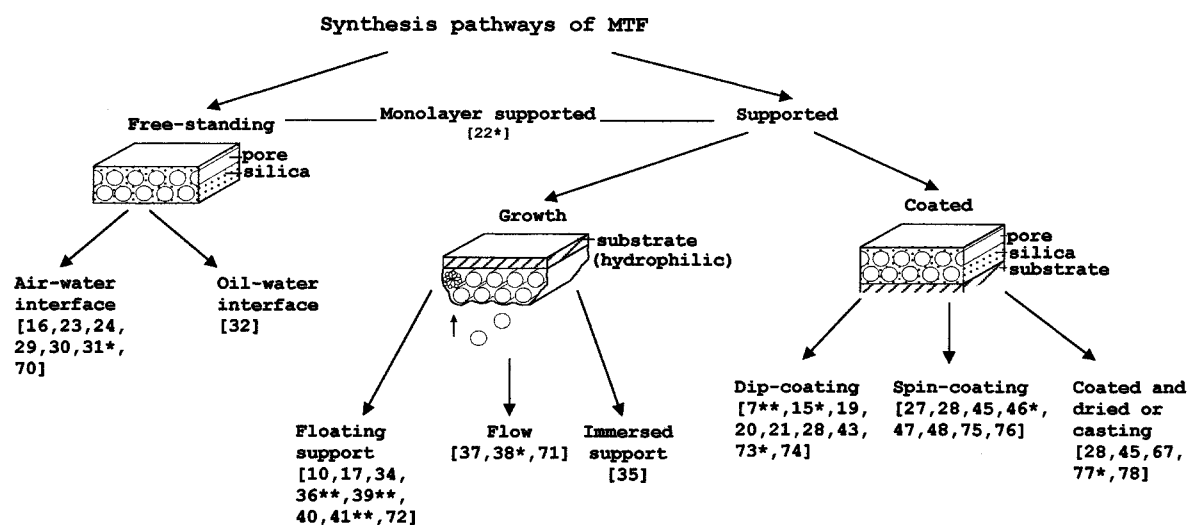


Fig. 1. Summary of different preparation methods of MTF.

the films nucleate around hemi-micelles of surfactant located at the air–water interface and grow by co-aggregation of the surfactant and silica into the water phase.

The first films obtained at the air–water interface exhibited hexagonal pore symmetry with the pores aligned parallel to the interface. This orientation is the more probable one, as it results from aggregation of micelles in the interfacial plane, rather than in the direction normal to the interface. However, this orientation reduces the accessibility of the pores to guest molecules, and thus their usage in applications such as catalysis. Pore-accessibility is highly enhanced in structures which possess three-dimensional symmetries (e.g. bicontinuous cubic, Ia3d) and by pore alignment in the direction normal to the interface. The former was achieved by the use of gemini surfactant (two-tailed surfactants separated by a spacer) as the templating moiety resulting in a three-dimensional hexagonal phase ( $P6_3/mm$ ) [29,33]. These films were stable upon calcination [29]. Another research group [31•] used glycerol or polyethylene glycol to stabilize micellar cubic phase (these films were not calcined). Films formed at the oil–water interface exhibited hexagonal symmetry with the pores oriented perpendicular to the interface [32].

The presence of a lipid monolayer at the air–water interface was found to accelerate the formation of MTFs due to interactions between the lipid head-groups and the surfactant and silica aggregates [22•]. These films may be considered as ‘semi-supported’.

## 2.2. Solid supported mesoporous thin films

MTFs were formed on different types of solid supports by a variety of preparation methods (Fig. 1). The methods may be classified by the role played by the surface in the growth process. Thus, we distinguish between surfaces which nucleate MTF growth, and

surfaces which are coated by the film. In the first case film growth is slower than the latter.

### 2.2.1. Films grown on supports

The first attempt to grow films on a solid support (Fig. 1) was reported by Yang et al. [34]. The films were grown on mica, and exhibited hexagonal ordering with the pores aligned parallel to the support (Fig. 2). Typical film thickness varied from 0.2 to 1  $\mu\text{m}$  for growth periods of 1 h to 1 week, respectively. The films could be prepared also on hydrophobic, amorphous and stainless steel [35] supports. The specific interactions of the surfactant molecules with the support were observed to affect the structure of the resulting films. For example, surfactant molecules that form hemi-micelles on hydrophobic surfaces and spheroidal or elongated micelles on hydrophilic surfaces induced growth of MTFs with different structures: MTFs grown on mica (hydrophilic, crystalline) were distorted hexagonal [17], while those grown on graphite (hydrophobic, crystalline) consisted of rigid parallel strips [17]. In both cases the pores were aligned parallel to the surface. In MTFs grown on amorphous supports [17] the pores were aligned perpendicular to the support and the film exhibited distorted hexagonal packing. Moreover, it was observed that films grown on crystalline substrates exhibited in-plane orientational ordering of the surfactant rods. On graphite [10,17] and mica [17,34] the surfactant rods were parallel to the *c*-axis of the support. Yet, it was found that crystalline surface is not sufficient for inducing preferential orientation [36••]: for thin film growth on single-crystal silicon wafers, preferred orientation was observed only on (110) wafers, probably due to the higher anisotropy of this plane.<sup>2</sup>

Microsize alignment could also be obtained by macroscopic actions: i.e. directional flow (Fig. 1) of the reagent solution [37,38•], or covering the original substrate with ordered polymer thin film [39••]. Alternatively, rubbing of a substrate covered with amorphous polymer film [40,41••] resulted in ordering of the polymer chains and induced MTF orientation.

### 2.2.2. MTFs formed by coating

Conventional methods for thin film formation, i.e. spin- and dip-coating, were applied for preparation of MTFs. In these methods an oligomeric solution of silica is prepared prior to the addition of surfactant. In many cases, coating is carried from a solution

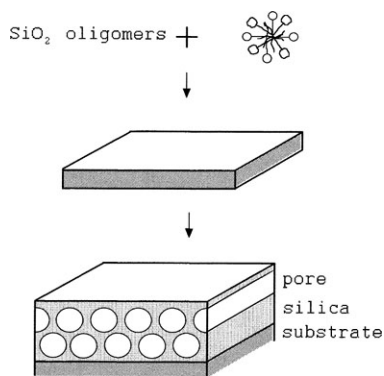


Fig. 2. Mechanism of MTF formation at support–water interface (adopted from Ogawa [46•]).

<sup>2</sup>This type of surface induced orientation is often described as ‘epitaxial growth’. However, the authors of this review find this term misleading as it implies crystallographic matching between the pore structure and the crystalline structure of the substrate, which does not exist here.

containing a highly volatile liquid so as to enhance the rate of film formation by rapid solvent evaporation. Preparation of thin films by sol-gel techniques was reviewed by Brinker et al., some of them excluded MTFs [42] and others included them [43,44].

### 2.2.3. Spin-coating

MTF formation by spin-coating was first reported by Ogawa [45]. The films were found to be stable upon calcination with surface area greater than 1000 m<sup>2</sup>/g. A few years later the same author inferred that the pores of the hexagonally ordered film are parallel to the substrate [46,47] (similar to films grown on support or at air–water interface). The pore diameter could be controlled by surfactant chain-length as in bulk materials. In MTFs with lamellar ordering, silica/surfactant ratio was found to control the wall thickness of the silica [48]. This dependence is unique to MTFs and was not reported for bulk mesoporous materials.

Macroscopic cracks which were observed in films prepared by spin-coating could be prevented by pretreatment of the glass support with aluminium hydroxide [27]. It was suggested that the pretreatment invokes covalent bonds between the film and the substrate, and thus improves the adhesion of the film to the support.

While quite a few successful attempts to produce spin-coated MTFs were reported, detailed characterization of surface parameters of the films, as well as their continuity and microstructure were only discussed by Martin et al. [28]. In this work, base

catalyzed hydrolysis of silica was used while in most of the reported studies acidic conditions were employed.

With the exception of spin-coating, formation of mesoporous materials by different methods was investigated in situ: dip-coating [19–21,43], film growth [23] or bulk [49–55].

### 2.2.4. Dip-coating

The formation of dip-coated films was monitored in situ using fluorescence measurements. The structure of the surfactant [19–21,43] and silica frameworks [19] were investigated in situ, while interferometry was employed for measuring the film thickness [20,21]. Solvent evaporation which increases the concentration of the solution to above the critical micellization concentration (CMC) value [20,21] was found to induce mesophase formation during the coating process itself [21]. At the same time, the thickness of the film continuously decreases [20,21].

Different symmetries in dip-coated films were reported: one-dimensional hexagonal [20,21] (pores parallel to the surface), two- and three-dimensional hexagonal [15,21], lamellar [20,21] and cubic [15,21], depending on the initial surfactant concentration [15,21] and surfactant type [15]. It was found that surfactants with a large polar headgroup lead to the formation of materials with three-dimensional symmetries [15].

While the materials described above have the pore diameter less than 4 nm, Zhao et al. used triblock copolymers [7] to produce thin films with accessible pores up to 9 nm in diameter.

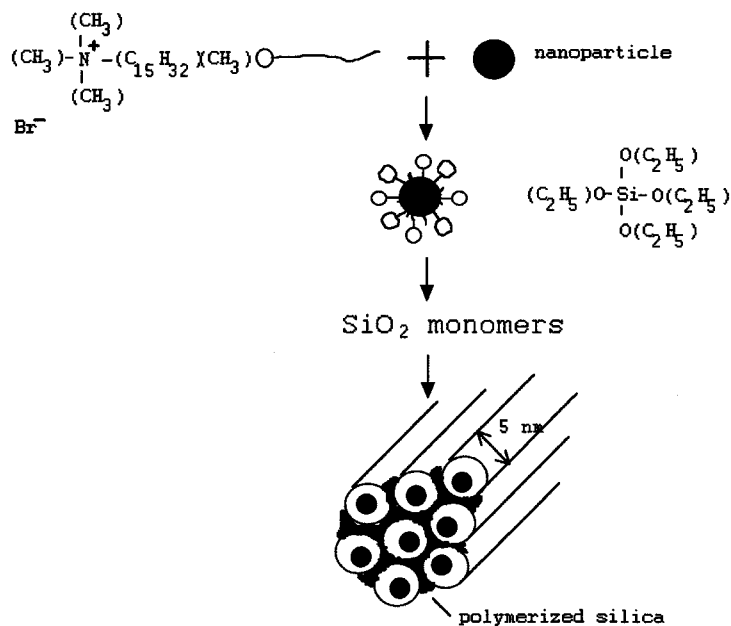


Fig. 3. Schematic presentation of eMTF formation.

### 2.3. Mesoporous silica films with metal nanoparticles

An additional aspect of MTFs is their use as a hosting matrix for nanoparticles. Embedding of nanoparticles into thin films (eMTF) (Fig. 3) opens a new field of applications, which rely on quantum size effects of the confined particles. During the last decade it was found that magnetic ferrosmectic [56] and metallic [57] nanoparticles can be incorporated into lamellar [58] as well as hexagonal [59] liquid crystalline phases (LCP). In the ordered phases, the efficiency of embedding was maximal when the particle diameter (in the range of 3–10 nm) was smaller (approx. 60%) [59] than the relevant liquid crystalline spacing. In other studies the particle size could be as large as the interlayer spacing [57]. LCP spacing could be enlarged via swelling [59], and thus enables the incorporation of larger particles.

It was recently demonstrated for bulk mesoporous material that it is possible to embed  $\text{Fe}_2\text{O}_3$  [60] or GaN [61•] nanoparticles by impregnation. Pre-formed nanoparticles of Pt or Pd capped by triblock copolymer [62•] were embedded in the pores of the bulk mesoporous material during the templating process [62•]. CdS nanoparticles capped by small-molecule surfactants were introduced into the pre-formed mesoporous material at the post-synthesis stage [63].

The publications mentioned above are few examples of mesoporous hybrids of silica matrices embedded with particles which were prepared in the *bulk*. A procedure involving impregnation of nanoparticles within dip-coated MTF was applied recently to silver [64••] nanoparticles. The eMTF could be used as insulator or as conductor [65].

MTFs can be ‘embedded’ by the templating molecules themselves: functionalization of the surfactant molecule could result in enhanced conductivity [65] or improved catalytic activity [66]. Swelling the templating micelles with hydrophobic functional molecules is yet a different way to prepare optically active MTF (addition of functional silane derivative) [67] or new laser fibers (addition of rhodamine) [68]. Since one could include a wide range of nanoparticles, the nature of the mesoporous material could be controlled by the formation of such hybrid system.

Trapping or coating of molecules over the mesoporous channels [69], as well as loading of framework molecules are beyond the scope of this review and will not be described here.

### 3. Conclusions

Since their discovery, mesoporous materials were the subject of a large scientific effort, aiming towards better understanding of their formation, structure and the origin of their activity, leading to judicious utilization of MTFs in a variety of technological applications. In this review we surveyed the large variety of methods which are currently applied for the preparation of MTFs. The different protocols are distinguished by the way they impose the formation of a thin film. These could be a large surface-to-volume ratio of the reactive solution, limited reservoir of material or a strong effect of surface forces leading to orientational ordering. MTFs obtained by the different preparation methods are commonly characterized by hexagonal ordering with pores oriented parallel to the interfacial plane and high surface area. The MTFs are distinguished by the degree of continuity, pore alignment and surface roughness.

We envisage that the production of mesoporous materials in a thin-film geometry will lead to their integration in advanced applications. For example, MTFs can replace non-porous silicon-dioxide as the standard insulating layers in nanoelectronics: porosity reduces the dielectric constant of the material relative to that of silicon oxide,<sup>3</sup> while retaining the high thermal stability, good mechanical properties, low ion contents and additional properties that have made silicon oxide the ultimate material for isolating layers. The ability to functionalize the films and trap nanoparticles within the pores opens new possibilities for application as sensors, non-isotropic conductors, and matrices for optically, magnetically and electrically active materials. We believe that in the near future, a whole wealth of new applications for MTFs and eMTFs will emerge, together with a better understanding of their formation and control of their structure and properties.

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