MESOPOROUS THIN FILMS: PROPERTIES AND APPLICATIONS

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Abstract. Mesoporous films are a fine example of a self-assembled nanosystem, containing ordered porosity in the 2–50 nm range. A great number of characteristics, including framework nature (composition, crystallinity), high surface area, pore dimension, shape, surface, accessibility and pore array symmetry and interconnection can be tuned using green chemistry synthetic techniques. These materials present potentials in several fields where a large functional interfacial area contained in a robust framework is required. The capability of changing in a separate way the characteristics of the inorganic framework and the pore surface leads to an amazing potential in tuning functional properties, due to the combined properties of a thoroughly tailored pore system and the inherent features of thin films. These properties can be tailored to respond to changes in the environment, such as relative humidity, making mesoporous hybrid thin films an exciting prospect for several nanotechnology applications (e.g. sensors, actuators, separation devices). Here we present some basic concepts revolving around mesoporous films. We will first comment on the synthetic approach in the fabrication of these materials. Second, we will discuss the aspects regarding template organization and surface functionalization. Third, we will review some applications illustrating the potentialities of theses self-assembled nanomaterials.

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1. Sol-Gel Chemistry, Self-Assembly and Mesoporous Thin Films

1.1. INTRODUCTION

Sol-gel processing is a low temperature synthesis route that is particularly suitable for the deposition of thin films from a liquid phase.[1] The high versatility of the technique has allowed a wide diffusion in different fields of applications and several products are now on the market.[2] The soft chemistry approach of sol-gel has known a renewed interest because of the recent boom of nano-science; sol-gel processing has emerged as one of the most interesting routes to bottom-up preparation of nanomaterials, nanoparticles and surface functionalization of nanostructures.

Two main different approaches to sol-gel nanochemistry can be envisaged. In the first one sol-gel reactions are used to obtain interconnected structures through polycondensation of the precursors, which is the typical bottom-up route for thin and ultra-thin film preparation. In the second one the final material is obtained through an intermediate step by using sol-gel chemistry for the syn thesis of nano-objects, such as nanoparticles or nano-building blocks (NBBs).[3] Sol-gel chemistry can be, however, also combined with more sophisticated nanosynthesis techniques to get ordered and hierarchical structures. Controlled porosity in a material can be achieved, for instance, by templates that are removed after the preparation; templates of different dimensions can give hierarchical porous materials.[4] Porosity in the nano-scale is an important property of a material that should find its field of applications in nanotechnologies.

Micro- (<2 nm), meso- (2–50 nm) and macro-porosity (>50 nm)[5] can be used to entrap organic functional molecules, to create nanoreactors or as host for nanoparticles.[6] The properties of porous materials can be greatly enhanced if an organized and interconnected porous "structure" is obtained, in this case diffusion, adsorption and entrapping of functional molecules are favored and the material can reach a high level of sophistication. Mesoporous ordered materials are an important example of this type of nano-engineered materials whose synthesis is achieved through a combination of sol-gel and supramolecular chemistry.[7,8] The formation of an organized array of pores, whose topology, size and distribution is controlled by the processing parameters, is obtained through a self-assembly process. Amphiphilic molecules, such as ionic surfactants and block copolymers, are used to generate organic micelles that serve as the templates; removal of the micelles leaves ordered pores (Figure 1).

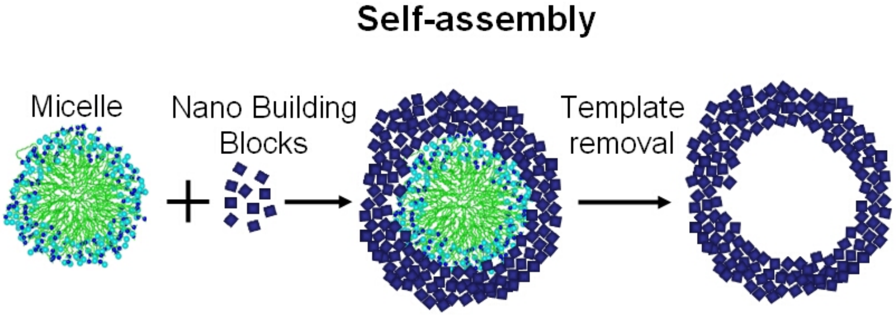

Figure 1. Schematic picture of the condensation of the nanobuilding blocks on the micelle surface.

The micelle formation and their organization is driven by solvent evaporation, and in the particular case of thin mesoporous films this process is specifically indicated as evaporation-induced self-assembly (EISA).[9,10] Even if several details of self-organization need to be studied, the overall process of self-assembly is quite well understood. The control of the kinetics of the different reactions and processes involved in EISA plays the main role. Several parallel processes are involved in EISA: film formation upon solvent removal, template-NBB self assembly and inorganic condensation. Controlling of the mutual interactions and kinetics is very important to avoid phase separation and to obtain an organized templated mesostructure. The variables that affect self-assembly are different from those used in the preparation of mesoporous pow-ders and monoliths, such as MCM-41, the first one to be synthesised by Mobil researchers.[11,12] Many parameters such as withdrawal rate, relative humidity and temperature in the deposition room, must be controlled very carefully. By this technique it is possible to fabricate different types of mesoporous ordered thin films, the most common are silica, transition metal oxides, hybrid inorganic-organic oxides, phosphates or carbon mesoporous films.

Due to their properties, mesoporous materials have found important applications in several emerging fields: the high specific surface area, composed of well-ordered tunable porosity within the 2–50 nm range, and the possibility to functionalize this large surface is an important feature of mesoporous organized thin films; they can be used for immobilizing guest molecules, such as biomolecules and functional organic molecules.[13–14] The pores can be also used as nano-reactors for the in situ growth of nanosized objects,[15,16] or as preferential adsorption sites in catalytic and sensing applications. The large number of publications and patents in different fields such as microelectronics, photonics, optoelectronics, electrochemistry and biosensing are witnessing the potentialities of these materials.

1.2. SELF-ASSEMBLY IN MESOPOROUS THIN FILMS

Self-assembly of mesoporous thin films could appear a quite simple process if we look only to the preparation protocol. A typical synthesis is based on sol containing an alkoxide or an inorganic salt as inorganic precursors, and a surfactant or an amphiphilic block copolymer as the structure-directing agent. Self-assembly is, however, achieved through a delicate balancing of the different processes: the polycondensation reactions of the precursors that will form the species condensing at the micelle surface, the micelle formation and the formation of a hybrid interface. Solvent evaporation pushes the micelle formation and their organization, leading to the formation of an organized array of templating micelles into a periodic mesophase. At the same time, the sol-gel reactions give rise to the formation of an interconnected network that contains the organic ordered mesophase. The organic template is then removed either by thermal decomposition or by chemical extraction, and leaves an ordered array of pores which reproduces the micelle arrangement in their size, shape and relative spatial location. Post-treatments on mesoporous films are used for chemically grafting of functional molecules or to enhance the stability of the film.[17]

The sol-gel chemistry plays its major role to form the chemical species that will self-assemble and finally condense on the micelle surface. A cluster of condensed species of nano-dimension, which is obtained by controlling the polycondensation of inorganic molecular precursors in mild temperature conditions is, in general, the product of the sol-gel synthesis.[18,19] The choice of the organic solvents, the pH and the amount of water directly affect the process. The choice of the pH value is a critical parameter because if the polycondensation reactions are too fast with respect to the micelle formation and assembly, the global self-organization process will fail. In silica-based systems, the pH is generally set near the isoelectric point ($pH_{iep} \approx 2$): in this way, the inorganic colloids in the solution do not aggregate and the solution can be stable even for several months. In general, both hydrolysis and condensation have to be controlled and optimised, to obtain small hydrophilic silica-derived nano-objects.[13] For transition-metal oxide precursors, hydrolysis and condensation are fast, and extended condensation is avoided only in highly acidic media, lower than $pH < 1$. In these conditions, using small hydrophilic clusters as NBBs results in good ordering.[20,21]

The "*race towards order*" gives organised structures only if the kinetic constants of the process are in this order:

$$k_{inter} > k_{org} > k_{inorg}$$

with k_{inter}, k_{org} and k_{inorg} the relative rates of interface formation, organic array assembly and inorganic polycondensation, respectively. The condensation of the inorganic clusters must be slowed down enough, in order to avoid that an extended polycondensation before the appearance of an interface and formation of the micelles stop self-assembly.

The overall self-assembly process to obtain an organized mesoporous film is based therefore, on co-assembly of inorganic clusters to form an interconnected framework (the pore walls) with the template in an adequate balance of the different kinetics. 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 reaches as much as several hundreds of square meters per gram.[22] An important fraction of the energy towards stabilization of a mesostructured material arises from favorable interactions of NBBs at the hybrid interface. Figure 2 shows an ideal representation of the Evaporation-Induced Self-Assembly that is observed during the deposition of thin films via dip-coating. It should be underlined that self-assembly is also observed if the films are deposited via spin-coating, spraying or casting. In the dip-coating, the substrate is immersed and withdrawn from a precursor solution containing the alkoxide, water, the solvent, the catalyst and the surfactant at concentrations lower than critical

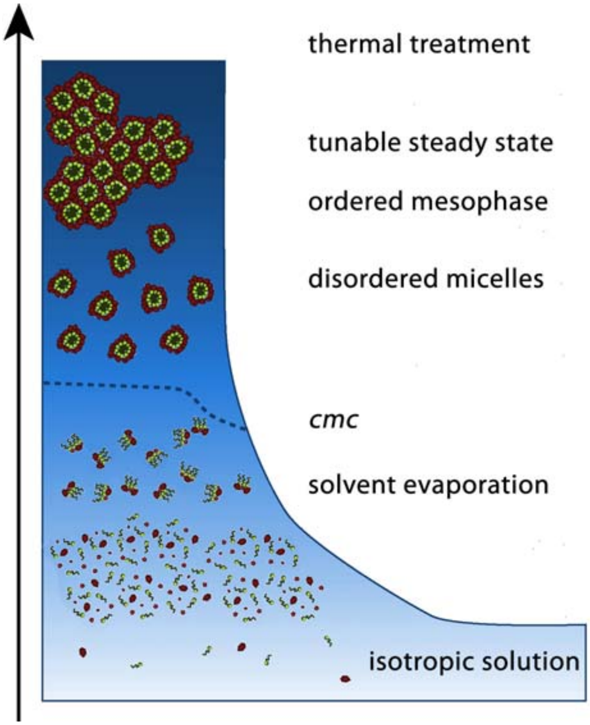

Figure 2. Self-assembly of mesoporous thin films during dip-coating.

micelle concentration, *cmc*.[23] Evaporation of the solvent (typically an alcohol such as ethanol) and water leaves a film that is enriched in nonvolatile species (inorganic and template). As soon as *cmc* is reached, the isolated surfactant molecules form disordered micelles within the film and in a second stage an ordered array. The organization of the micelles represents a templated order in the film, which can be disposed in several possible phases. Just as an example, several different ordered phases such as 2d-hexagonal,[24] cubic,[25] orthorhombic,[26] bicontinuous[27] and tetragonal[28] have been observed in silica films. A post-deposition thermal treatment is necessary to stabilize the structure, this is a delicate point because thermal induced shrinkage can change the mesophase (see Figure 3) and the pore shape, which typically shows an elliptical form upon shrinkage.[29]

Mesoporous thin films also exhibit a very peculiar property, *tunable steady state*, which can be defined as a particular metastable stage during which it is still possible to change the mesophase by intervention from the external environment.[30] The ordered arrays of the micelles is changed by variations of the relative humidity that induces a controlled swelling of the micelles. The ordered mesophase can be also disrupted and restored by X-rays, reversible order-disorder transitions have been observed in hafnia films.[31]

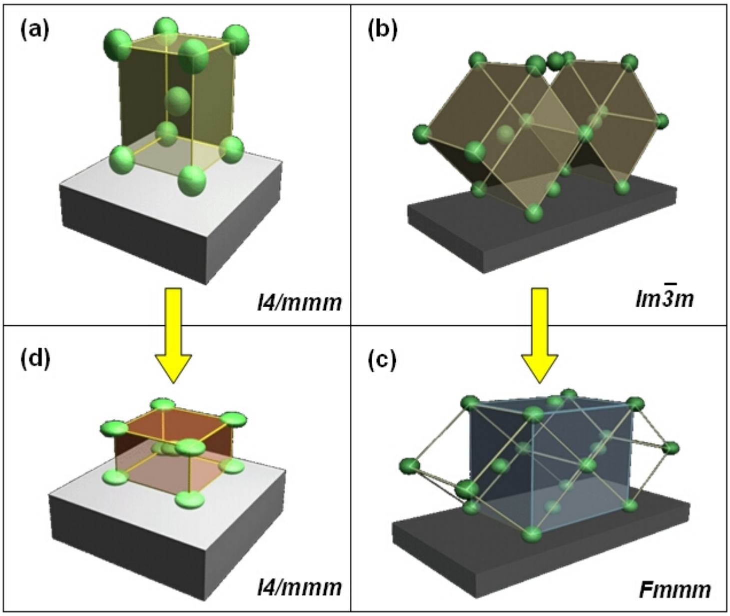

Figure 3. Changes in the mesophase induced by thermal shrinkage.

2. Morphology and Functionalization of the Pore Surface

2.1. ORDER-DISORDER IN MESOPOROUS FILMS

Another fascinating aspect of self-assembled mesoporous films is associated to order and disorder. As we have seen, the "race towards order" that governs the self-assembly process is driven by the solvent evaporation. The final material, after film deposition, is a system in which an ordered array of micelles is entrapped in an interconnected backbone. The consolidation of the framework and the removal of the template leave a porous ordered mesostructure, where the order is in the porous phase. The possibility to observe order in the pore walls, i.e. crystalline structures, depends on composition and processing conditions. Silica films give only amorphous pore walls; it seems impossible, at least at the moment, to obtain crystalline silica structures of any phase in the pore walls of mesoporous films. Other oxides, such as titania or hafnia, at the proper temperature of treatment form nano-crystals in the pore walls, in general, at temperatures that are low enough to avoid collapse of the mesostructure.[32,33] It should be underlined that in any case these mesoporous films show a surprising stability at high processing temperatures. Mixed oxide mesoporous films, such as perovskite have been also obtained, by using templates with enhanced solubility difference among their hydrophilic and hydrophobic regions.[34]

In mesoporous films we have, therefore, two possible degrees of order, one is correlated with the porosity and the other with the framework that forms the pore walls. The first case is represented by an ordered mesoporous film with amorphous pore wall, which is actually the case of silica or other oxides if the processing temperature is not high enough to produce a crystalline phase. The case of silica is, however, very intriguing and the reason why we could not yet be able to get an ordered phase with crystalline walls is challenging several researchers in the field.[35] The particular processing conditions that are used for self-assembly of silica films (the low pH) can produce, however, an intrinsic formation of middle range ordered nano-structures, such as four-fold and three-fold rings at least. This case has been well documented by several researcher and is an intermediate case of order-disorder in silica mesoporous films, the pores are ordered, the pore walls are amorphous but a medium range order (the silica rings) is observed. This is not just an "academic" classification because it has been demonstrated that the presence of silica rings in the pore walls strongly influences the mechanical properties, such as the elastic modulus.[36] The third case is represented by ordered porous films whose pore walls are crystalline. In this case nanocrystalline domains of different orientations form the material framework. The last case is also peculiar of mesoporous materials, even if not yet reproduced in films, which is the formation of an ordered hybrid organic-inorganic structure in the backbone. This has been reported by Inagaki and coworkers for mesoporous powders and can be observed if the organically modified alkoxide precursor is a bridged silsesquioxane.[37]

2.2. MONOCRYSTALS – POLYCRYSTALS

The organization of the pores within a mesoporous films is achieved through self-assembly and the mesostructure that is formed is governed by the chemical-physical parameters of the process. We have seen that the concept of order is very important in mesoporous films and that several types of ordered nanostructures can be found. In general, the ordered arrays of micelles, or, after template removal, the ordered porous structures that are observed, can be described using crystallographic tools in terms of a "crystal-like" phase.

There is a good correspondence between the phases that can be indexed by small angle X-ray scattering (SAXS) and TEM and the crystalline structures of the phase group. The variation of the electronic density that is measured by SAXS allows indexing the mesostructure such as a crystalline-like phase. In general, detailed SAXS measurements in grazing and normal conditions determine that there is a polycrystalline distribution of mesoporous domains, which are well oriented along the substrate (i.e., the *z* direction), but present all possible orientations in the *x-y* plane (Figure 4). This feature is commonly known as *planar disorder*.

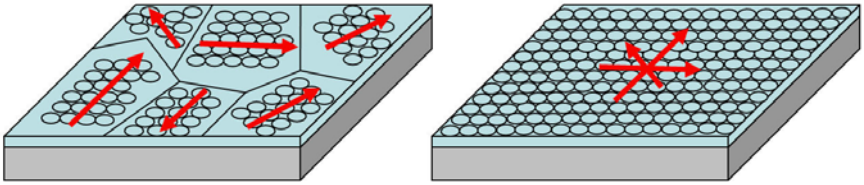

Figure 4. "Polycrystal"- and "monocrystal"-like porous structures.

Detailed TEM analysis shows grain boundaries at the mesoscale.[38] The preparation of a "monocrystal", in which the order is extended on the whole film, or at least on a longer scale (mm to cm) can be carried out by depositing the mesoporous thin film on a polymeric substrate which has been pre-patterned by rubbing.[39] This perfection is however hard to achieve. Another point is the quality of the ordered phase that can be obtained. Some studies have shown that defects, similar to those observed in metallic crystalline structures can be formed, such as stacking faults and dislocations.[40] Controlling the order and the defects is however possible, as shown by some researchers that obtained "mono-crystals" like films and "defect" free mesoporous films.[41] It is, however, important to be aware that in most cases it is quite difficult to control defects in the porous phase and to obtain an extended organization (from a micron scale up to centimeters).

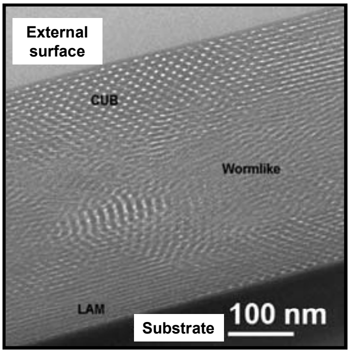

Figure 5. TEM image of a section of a mesoporous silica film, different mesophases can be identified.

The TEM image in Figure 5 shows a cross-section of a mesoporous silica film, the light regions of the sample are the pores. Specific domains of different phases are observed in this sample; in particular, a lamellar phase is formed at the bottom of the film, closer to the substrate, worm-like disordered domains can also be identified in the middle of the films and a cubic ordered phase is located close to the external surface.

2.3. PORE SURFACE FUNCTIONALIZATION

The large reactive surface area is one of the most interesting features of mesoporous films. Silica mesoporous films show a high silanol coverage of the pore surface even after a mild thermal treatment to stabilize the mesostructure.[42] The presence of silanols on the mesopore surface can be used to graft organic functional molecules to add specific properties such as the capability of adsorbing heavy metals or sensing species.[43,44]

Surface functionalization can be achieved mainly by two different routes that are generally indicated as "one pot" and post functionalization. In the first case an alkoxide (or a metal salt) is co-reacted with an organically modified alkoxide to add the functional species. By this type of approach the functional group will reside on the external surface of the pores, with the exception of the synthesis that employs a type of organically modified alkoxides, bridged silsesquioxanes (Figure 6).[37] In this case the organic groups will be part of an interconnected hybrid organic-inorganic network that forms the backbone of the mesoporous films. Post grafting is another viable route, after deposition the film is functionalized by immersing in a solution (a typical example is 3-aminopropyltriethoxysilane in toluene) containing the organically-modified alkoxide.[14] Functionalization is, however, not a trivial process and a full control and reproducibility, especially in the case of post grafting, is still quite difficult to achieve.

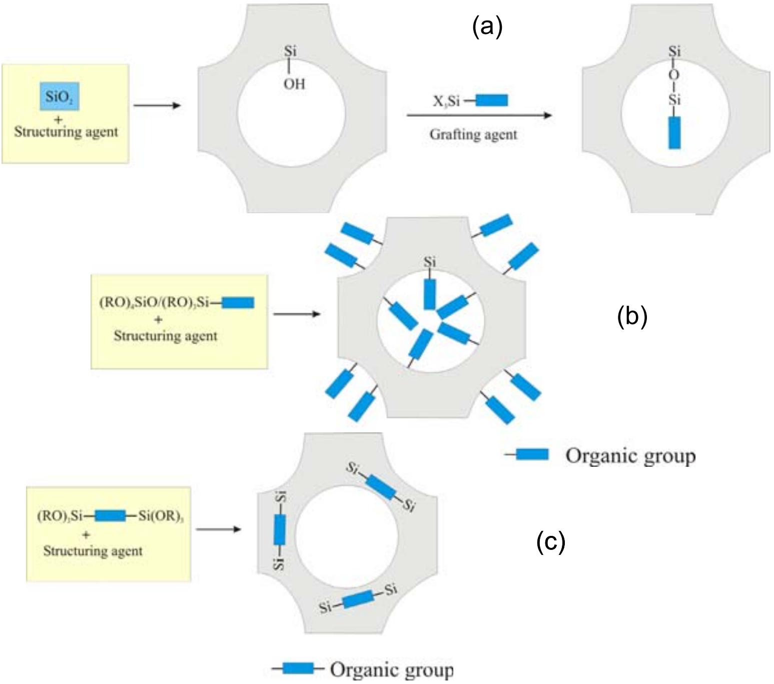

Figure 6. Pore surface functionalization: (a) post grafting; (b) “one pot” route; (c) “one pot” with bridged silsesquioxanes.

3. Applications of Mesoporous Films

3.1. HUMIDITY SENSORS BASED ON MESOPOROUS SILICA THIN FILMS

The importance of pore surface and the presence of silanols (in silica based mesoporous films) or -OH groups in other materials is shown by the properties of the films that are achieved by controlling the pore surface. An interesting example is the response of silica mesoporous films to changes of relative humidity in the external environment.[45] Humidity and alcohol vapor sensor devices are fabricated using mesoporous silica thin film as sensitive membranes. The films have shown a very different sensitive response with respect to non-mesoporous silica sol–gel thin films used as reference in testing measurements. In general, silica dense films do not show any electrical response and are not used for sensing applications, but in the case of mesoporous silica the high silanol coverage allows activating a protonic conducting mechanism of the "Grotthus" type and work well as simple humidity sensors (Figure 7).

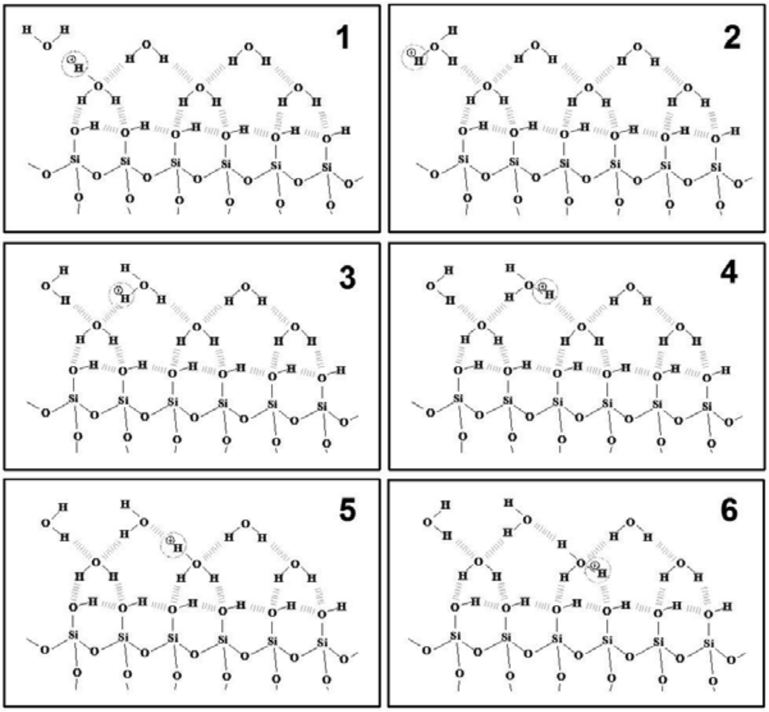

Figure 7. Schematic drawing of a the "Grotthus" model applied to mesoporous silica films.

The mesophase is easily accessible by the external environment and increases the performances for sensing applications. A strong response has been observed in continuous current in mesoporous silica films that have been treated to 350°C; this temperature is high enough to remove the template and stabilize the mesostructure. The films deposited on an interdigited circuit have shown a fast and reproducible electrical response whilst dense sol-gel silica films did not exhibit

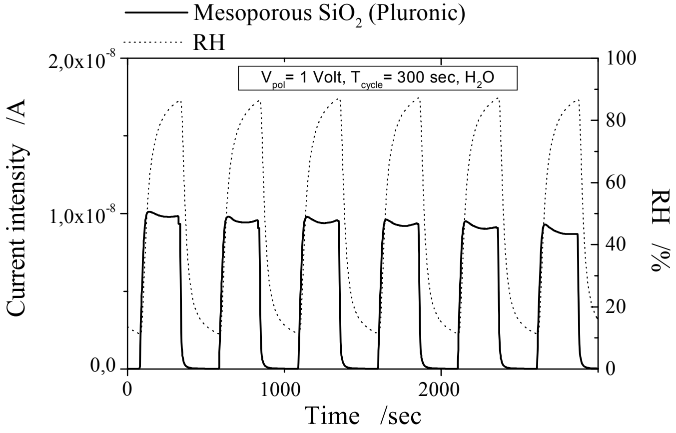

Figure 8. Electrical response of a mesoporous thin films to cyclic changes of relative humidity from the external environment.

any change (Figure 8). A good reproducibility of the electrical response and a different response as function of the surfactant used as templating agent have been observed.

3.2. MESOPOROUS TITANIA FILMS FOR DYE-SENSITIZED SOLAR CELLS

Mesoporous titania materials have important applications in photocatalysis, electrochemical sensors and photovoltaic devices. Mesoporous films prepared by wide-band gap semiconductor oxides, such titania, niobia or tantalia and formed by interconnected nanocrystalline particles allow, in fact, an efficient charge carrier transport. The interface between the organic dye and the surface of the titania mesoporous walls forms a heterojunction where photo-induced charge transfer separation is observed. By filling the mesopores with a proper liquid hole conductor (usually a solution containing the redox couple I^-/I^{3-}), a heterojunction with a very large contact area will be formed. If the formation of an interconnected network of oxide nanocrystals is crucial for electronic conduction, oxide porous films with a large surface area and controlled pore organization are expected to add a significant improvement to the overall performances of a dye-sensitized solar cell (DSSC) device. The presence of an organized porosity within the films can, in fact, allow the formation of highly controlled morphology that facilitates the electronic conduction. Mesoporous channels organized with a preferential orientation that is normal to the substrate will give, therefore, one of the best configurations for DSSC materials.

Since the discovery of organic-sensitized photovoltaic devices, the utilization of nanocrystalline anatase electrodes is a standard in the Grätzel-type solar cells.[46,47] The DSSC combines the high light absorption of a specifically designed organic dye with the electronic conductivity of a nanocrystalline anatase network. Several papers have reported systematic studies about the optimal conditions to prepare thick titania layers by screen-printed (or doctor-bladed) colloidal solutions;[48,49] using this technique, the typical thickness of nano-crystalline anatase electrode is 1–10 µm. The control of the synthesis parameters in the EISA technique allows obtaining thick films via multiple dip-coating, this process does not disrupt the organization of the pores in the single layers and the structure of the porous phase is maintained even after removal of the organic template. Controlled crystallization of the amorphous titania pore walls into crystalline anatase, whose crystallite dimensions can be adjusted within a certain degree as a function of the processing conditions, is attained through thermal calcination. Thermal treatments at temperatures between 400°C and 600°C give a high surface area mesoporous nano-anatase coating presenting channel-voids very interesting for dye-sensitized solar cells.

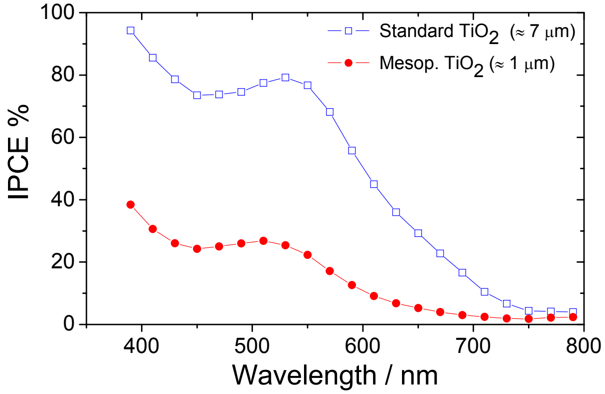

Figure 9. Photoaction spectra of a 1 µm thick mesostructured titania film (calcined at 350°C) compared with a 7 µm thick TiO_2 reference electrode. The incident photon current conversion efficiency is shown as a function of the wavelength. The two samples are both sensitized by N3.

In order to improve the control of morphology of TiO_2 electrodes for DSSC applications, mesostructured titania films have been prepared by EISA.[50] These films are composed of a continuous TiO_2 network of organized porosity that is partially crystallized. TiO_2 thick films, impregnated with a ruthenium dye, have been used to fabricate a DSSC device whose photoactivity have been tested.[51] The measurement of the incident-photon-to-current-efficiency (IPCE) of proto-typed solar cell based on titania mesostructured films (Figure 9) showed that this mesostructured material can be efficiently used, upon optimization of the thickness and processing conditions, as electrode in dye-sensitized solar cells.

3.3. X-RAY PATTERNING OF MESOPOROUS FILMS

The integration of bottom-up synthesized materials in devices requires a top-down processing.[52,53] Self-assembled mesoporous thin films are no exception, because specific patterning of mesoporous films in order to obtain circuits or dot arrays cannot be fulfilled by coating a substrate with the sol-gel film, without further processing.[54] In particular, the bottom-up route needs coupling with top-down processing such as substrate pre-patterning or film lithography.[55,56] In this way, hierarchically-structured materials can be obtained where organization resides on multiple length scales. The ordered mesopores are an ideal host for functional organic molecules or nanoparticles and the patterns, from the nano- to the micro-scale, allow designing devices for different types of advanced applications,[57] for example in DNA nanoarrays or lab-on-a-chip devices.

The possibility to pattern mesoporous films was first demonstrated by Brinker and coworkers, who employed a wide range of different several lithographic techniques. These were based either on mesophase change or on mesostructure disruption occurring upon irradiation with UV light. Alternatively, dip-pen nanolithography, ink-jet printing using a “self-assembling ink” and selective de-wetting were used to obtain patterned mesoporous arrays and micro-fluidic devices.

The possibility to pattern of mesoporous films was first demonstrated by Brinker and coworkers, who applied several lithographic techniques to fabricate patterned mesoporous films.[58,59] These techniques were based either on mesophase change or on mesostructure disruption occurring upon irradiation with deep UV light (wavelength 256 nm). Thin (max thickness 360 nm) films were patterned with a lateral resolution of 10 μm. Using an excimer laser (wavelength 248 nm) coupled with a phase mask, a resolution of around 560 nm could be reached. However, the use of a phase mask is restricted to the patterning periodical objects and is not suited for the fabrication of non-periodical structures. Alternatively, dip-pen nanolithography or ink-jet printing using a “self-assembling ink”, dip-coating and selective de-wetting were used to obtain patterned mesoporous arrays with high resolution (150 nm) and micro-fluidic devices.[60]

Photopatternable cyclic silsesquioxane compositions containing a photoacid generator were prepared, with the goal of achieving a photoresist-free porous low-dielectric constant precursor.[61] The films were patterned with a standard UV lamp (wavelength 350 nm), reaching a pattern lateral resolution on the micrometre scale (≈2 μm) with the possibility of patterning thick (1.3 μm) films.

A spatially-directed impingement of UV light (wavelength 187–254 nm) was demonstrated to be effective in selectively removing surfactant molecules from mesostructured thin films, generating patterns as small as 3 μm.[62] However, only thin (300 nm) films could be obtained, Immersion in a NaOH solution preferentially and completely etched the mesostructured material from the surface, leaving patterned mesoporous islands. This process was studied using optical microscopy, spatially resolved FTIR and spatially resolved ellipsometry.

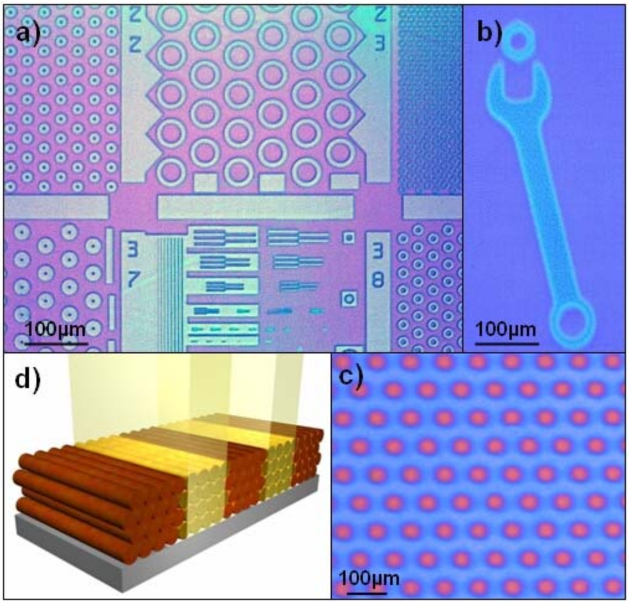

Figure 10. Optical micrograph of a patterned mesostructured silica film. The patterned objects can be discerned by their color, due to the difference in refractive index between the masked and the unmasked regions (a–c). Illustration of a mesostructured film subjected to DXRL (d).

Deep X-ray lithography (DXRL) can be used to pattern mesostructured silica thin films. DXRL is a manufacturing process by which a material that is exposed to high-resolution, high-intensity and extremely collimated synchrotron radiation through an X-ray mask changes its dissolution rate in a liquid solvent (developer). By this lithographic method, the mask pattern is, therefore, transferred to the material (Figure 10).[63]

This lithographic approach is based on selective template removal and silica polycondensation induced by synchrotron radiation. The areas of the film that are not exposed to radiation can be selectively etched due to a lower cross-linking degree of the inorganic network. An important advantage of this method is the possibility to simultaneously remove the surfactant and to induce condensation of the silica network in a single-step process.

Mesoporous pillars fabricated by DXRL were specifically functionalized by means of a dip-pen technique using the cantilever tip of an atomic force microscope (AFM). In a proof-of-concept experiment, the cantilever tip was used as a dip pen using rhodamine 6G as the ink in order to functionalize selected mesoporous pillars. The AFM cantilever tip was dipped into the rhodamine solution to take up a drop of solution, then it was approached to its destination pillar. When the tip landed on the pillar and the solution came into contact with the film, capillary forces drove the solution from the cantilever tip into the pillar, so that the mesopores became filled with the rhodamine solution. The results of this controlled writing process demonstrate that, using this method, it is possible to fabricate highly fluorescent mesoporous microstructures by the functionalization of micrometric mesoporous objects with different guest molecules (for example, oligonucleotide strands can be attached to the pillars in the fabrication of microarrays for DNA spotting). The lateral feature size of the patterned pillars corresponds to the conditions for microarray deposition, which are typically around 30 μm.[64] The lateral resolution of AFM enables functionalization of sub-micron mesoporous objects using small amounts of analytes; in addition, the patterned mesoporous support maximizes adsorption of guest molecules due to the high specific surface area of mesoporosity. Further-more, hexagonal p6 m mesostructures associated with cylindrical pores allow accessibility of the material from the outside and diffusion of analytical species into the material, opening the route for efficient immobilization of biological species in analytical applications.

4. Conclusions

Mesoporous thin films are an important class of bottom-up fabricated nanostructured materials. Evaporation-induced self-assembly allows preparing materials containing controlled ordered pores in the 2–50 nm range and with a number of functional properties. The high flexibility of the low-temperature and self-assembling route is a big advantage in designing materials with complex geometries and applications in advanced materials. Several applications have been demonstrated in different fields and high capability to integrate in the current technologies for photonics, sensors and electronics. The development of complex systems, such multifunctional hierarchical materials, based on mesoporous thin films is one of the main future directions of research in this field.

References

1. C. J. Brinker and G. W. Scherer, *Sol-gel science* (Academic, San Diego, CA, 1992).
2. *Handbook of sol-gel science and technology*, edited by S. Sakka (Kluwer AP, Dordrecht, 2004).
3. G. A. Ozin and A. C. Arsenault, *Nanochemistry: a chemical approach to nanomaterials* (The Royal Society of Chemistry, Cambridge, 1995).
4. D. Kuang, T. Brezesinski, and B. Smarsly, *J. Am. Chem. Soc.* 126, 10534 (2004).
5. J. Roquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger, *Pure and Appl. Chem.* 66, 1739 (1994).
6. M. Antonietti and G. A. Ozin. *Chem. Eur. J.* 10, 28 (2004)
7. G. Soler-Illia, C. Sanchez, B. Lebeau, and J. Patarin, J. *Chem Rev.* 102, 4093 (2002).
8. G. Soler-Illia, E. L. Crepaldi, D. Grosso, and C. Sanchez, *Curr. Opin. Colloid Interf. Sci.* 8, 109 (2003).
9. C. J. Brinker, Y. Lu, A. Sellinger, and H. Fan, *Adv. Mater.* 11, 579 (1999).
10. C. J. Brinker, *MRS Bull.* 29(9), 631 (2004).
11. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* 359, 710 (1992).
12. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am Chem. Soc.* 114, 10834 (1992).
13. G. Soler-Illia and P. Innocenzi, *Chem. Eur. J.* 12, 4478 (2006).
14. L. Nicole, C. Boissiere, D. Grosso, A. Quach, and C. Sanchez, *J. Mater. Chem.* 15, 3598 (2005).
15. S. Besson, T. Gacoin, C. Ricolleau, C. Jacquiod, and J. P. Boilot, *Nano Lett.* 2, 409 (2002).
16. M. D. Pérez, E. Otal, S. Aldabe-Bilmes, G. Soler-Illia, E. L. Crepaldi, D. Grosso, and C. Sanchez, *Langmuir* 20, 6879 (2004).
17. P. C. Angelomé and G. Soler Illia, *Chem. Mater.* 17, 322 (2005).
18. D. Grosso, F. Babonneau, P.-A. Albouy, H. Amenitsch, A. R. Balkenende, A. Brunet-Bruneau, and J. Rivory. *Chem. Mater.* 14, 931 (2002).
19. M. Klotz, A. Ayral, C. Guizard, L. Cot, *J. Mater. Chem.* 10, 663 (2000).
20. G. Soler-Illia, E. Scolan, A. Louis, P. -A. Albouy, and C. Sanchez, *New J. Chem.* 25 156 (2001).
21. E. L. Crepaldi, G. Soler-Illia, D. Grosso, F. Ribot, F. Cagnol and C. Sanchez, *J. Am. Chem. Soc*. 125, 9770 (2003).
22. D. M. Antonelli, *Microp. Mesop. Mater.* 30, 315 (1999).
23. J. N. Israelachvili, *Intermolecular and surface forces* (Academic, London, 1998).
24. (a) M. Ogawa and N. Masukawa, *Microp. Mesop. Mater.* 38, 35 (2000). (b) D. A. Doshi, A. Gibaud, V. Goletto, M. C. Lu, H. Gerung, B. Ocko, S. M. Han, and C. J. Brinker, *J. Am. Chem. Soc.* 125, 11646 (2003).
25. Y. F. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. L. Gong, Y. X. Guo, H. Soyez, B. Dunn, M. H. Huang, and J. I. Zink, *Nature* 389, 364 (1997).
26. P. Falcaro, D. Grosso, H. Amenitsch, and P. Innocenzi, *J. Phys. Chem. B* 108, 10942 (2004).
27. R. C. Hayward, P. C. A. Alberius, E. J. Kramer, and B. F. Chmelka, *Langmuir* 20, 5998 (2004).
28. P. Falcaro, S. Costacurta, G. Mattei, H. Amenitsch, A. Marcelli, M. Cestelli Guidi, M. Piccinini, A. Nucara, L. Malfatti, T. Kidchob, and P. Innocenzi, *J. Am. Chem. Soc.* 127, 3838 (2005).
29. P. Innocenzi, L. Malfatti, T. Kidchob, P. Falcaro, S. Costacurta, M. Guglielmi, G. Mattei, V. Bello, and H. Amenitsch, *J. Sync. Rad.* 12, 734 (2005).

30. F. Cagnol, D. Grosso, G. Soler-Illia, E. L. Crepaldi, F. Babonneau, H. Amenitsch, and C. Sanchez, *J. Mater. Chem.* 13, 61 (2003).
31. L. Malfatti, T. Kidchob, S. Costacurta, P. Falcaro, P. Schiavuta, H. Amenitsch, and P. Innocenzi, *Chem. Mater.* 18, 4553 (2006),
32. D. Grosso, G. Soler-Illia, E. L. Crepaldi, F. Cagnol, C. Sinturel, A. Bourgeios, A. Brunet-Bruneau, H. Amenitsch, P. -A. Albouy, and C. Sanchez, *Chem. Mater.* 15, 4562 (2003).
33. T. Brezesinski, B. Smarsly, K. Iimura, D. Grosso, C. Boissière, H. Amenitsch, M. Antonietti, and C. Sanchez, *Small* 1, 889 (2005).
34. D. Grosso, C. Boissière, B. Smarsly, T. Brezesinski, N. Pinna, P.-A. Albouy, H. Amenitsch, M. Antonietti, and C. Sanchez, *Nature Mater.* 3, 787 (2004).
35. N. Hedin, R. Graf, S. C. Christiansen, C. Gervais, R. C. Hayward, J. Eckert, and B. F. Chmelka, *J. Am. Chem. Soc.* 126, 9425 (2004).
36. H. Y. Fan, C. Hartshorn, T. Buchheit, D. Tallant, R. Assink, R. Simpson, D. J. Kisse, D. J. Lacks, S. Torquato, and C. J. Brinker, *Nature Mater.* 6, 418 (2007).
37. S. Inagaki, S. Guan, T. Ohsuna, and O. Terasaki, *Nature* 416, 304 (2002).
38. M. Klotz, P. A. Albouy, A. Ayral, C. Menager, D. Grosso, A. Vander Lee, V. Cabuil, F. Babonneau, and C. Guizard, *Chem. Mater.* 12, 1721 (2000).
39. H. Miyata, T. Suzuki, A. Fukuoka, T. Sawada, M. Watanabe, T. Noma, K. Takada, T. Mukaide, and K. Kuroda, *Nature Mater.* 3, 651 (2004).
40. X. Wu, K. Yu, C. J. Brinker, and J. C. Ripmeester, *Langmuir* 19, 7289 (2003).
41. P. Falcaro, S. Costacurta, G. Mattei, H. Amenitsch, A. Marcelli, M. Cestelli Guidi, M. Piccinini, A. Nucara, L. Malfatti, T. Kidchob, Tongjit, and P. Innocenzi, *J. Am. Chem. Soc.* 127, 3838 (2005).
42. P. Innocenzi, P. Falcaro, D. Grosso, and F. Babonneau, *J. Phys. Chem. B* 107, 4711 (2003).
43. L. Nicole, C. Boissière, D. Grosso, P. Hesemann, J. Moreau, and C. Sanchez, *Chem. Commun.* 2312 (2002).
44. (a) N. Liu, R. A. Assink, B. Smarsly, and C. J. Brinker, *Chem. Commun.* 1143 (2003). (b) N. Liu, R. A. Assink, and C. J. Brinker, *Chem. Commun.* 370 (2003).
45. A. Bearzotti, J. Mio Bertolo, P. Innocenzi, P. Falcaro, and E. Traversa, *Sens. Act. B: Chem.* 95, 107 (2003).
46. B. O'Regan and M. Grätzel, *Nature* 353, 737 (1991).
47. M. Grätzel, *Nature Mater.* 421, 586 (2003).
48. C. J. Barbè, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Ceram. Soc.* 80, 3157 (1997).
49. S. Burnside, V. Shklover, C. J. Barbe`, P. Comte, F. Arendse, K. Brooks, M. Grätzel, *Chem. Mater.* 10, 2419 (1998).
50. E. Lancelle-Beltran, P. Prené, C. Boscher, P. Belleville, P. Buvat, S. Lambert, F. Guillet, C. Boissiére, D. Grosso, C. Sanchez, *Chem. Mater.* 18, 6152 (2006).
51. L. Malfatti, P. Falcaro, H. Amenitsch, S. Caramori, R. Argazzi, C. A. Bignozzi, S. Enzo, M. Maggini, P. Innocenzi, *Microp. Mesop. Mater.* 88, 304 (2006).
52. C. J. Brinker and D. R. Dunphy, *Curr. Opin. Coll. Inter. Sci.* 11, 126 (2006).
53. J. Y. Cheng, C. A. Ross, H. I. Smith, and E. L. Thomas. *Adv. Mater.* 18, 2505 (2006).
54. H. Yang, N. Coombs, and G. A. Ozin, *Adv. Mater.* 9, 811 (1997).
55. D. Grosso, F. Cagnol, G. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, and C. Sanchez, *Adv. Funct. Mater.* 14, 309 (2004).
56. G. Soler-Illia, C. Sanchez, B. Lebeau, and J. Patarin, *Chem. Rev.* 102, 4093 (2002).
57. B. J. Scott, G. Wirnsberger, M. D. McGehee, B. F. Chmelka, and G. D. Stucky, *Adv. Mater.* 13, 1231 (2001).

58. D. A. Doshi, N. Huesing, M. Lu, H. Fan, Y. Lu, K. Simmons-Potter, B. G. Potter Jr., A. J. Hurd, and C. J. Brinker, *Science* 290, 107 (2000).
59. H. Fan, Y. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, V. Perez-Luna, G. P. Lopez, and C. J. Brinker, *Nature* 405, 56 (2000).
60. Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, and C. J. Brinker, *Nature* 410, 913 (2001).
61. Y. Y. Lyu, J. H. Yim, Y. Byun, J. M. Kim, and J. K. Jeon, *Thin Solid Films* 496, 526 (2006).
62. A. M. Dattelbaum, M. L. Amweg, L. E. Ecke, C. K. Yee, A. P. Shreve, and A. N. Parikh, *Nano Lett.* 3, 719 (2003).
63. E. W. Becker, W. Ehrfeld, P. Hagmann, A. Maner, and D. Munchmeyer, *Microelectron. Eng.* 4, 35 (1986).
64. M. Schena, *Microarray analysis* (Wiley-Liss, New York, 2003).