

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Sol-gel chemistry, templating and spin-coating deposition: A combined approach to control in a simple way the porosity of inorganic thin films/coatings

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1637567> since 2017-05-23T13:16:52Z

Published version:

DOI:10.1016/j.micromeso.2017.04.017

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in MICROPOROUS AND MESOPOROUS MATERIALS, 248, 2017, 10.1016/j.micromeso.2017.04.017.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.micromeso.2017.04.017

The publisher's version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S1387181117302573>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/>

Sol-gel chemistry, templating and spin-coating deposition: a combined approach to control in a simple way the porosity of inorganic thin films/coatings

Roberto Nisticò^{a,1*}, Dominique Scalarone^{a,b}, Giuliana Magnacca^{a,b}

^a University of Torino, Department of Chemistry, Via P. Giuria 7, 10125 Torino, Italy

^b NIS Centre, Via P. Giuria 7, 10125 Torino, Italy

¹ Now at: Polytechnic of Torino, Department of Applied Science and Technology DISAT, C.so Duca degli Abruzzi 24, 10129 Torino (Italy).

*Corresponding author. E-mail: roberto.nistico@polito.it, Tel. (+39)-011-0904745, Fax: (+39)-011-0904624

Abstract

Porous materials are powerful functional devices that can find applications in many fields, from nanotechnology to biomedicine, from catalysis to membrane separation. In general, porous materials can be processed in various forms, but a rising interest is growing around inorganic thin films and coatings, due to the increased number of applications based on their use. Among the different strategies proposed till now for preparing inorganic porous thin layers/coatings, a simple and versatile route consists in the combined use of sol-gel chemistry, templating, and spin-coating deposition. Therefore, in order to provide a helpful toolbox for users, an extended discussion around the physico-chemical principles behind each of these steps is here reported, also highlighting the advantages and disadvantages of each procedure, together with critical points.

Keywords: Amphiphilic block-copolymers; Coatings; Membrane technology; Mesoporous materials; Soft-templating; Sol-gel; Spin-coating; Thin films.

1. Introduction

According to the IUPAC definition, porous materials are divided into three classes named respectively: micro- (with pore width less than 2 nm), meso- (between 2 and 50 nm) and macroporous (over 50 nm) materials [1-2]. Porous materials have been widely studied in the past and they are still attracting the attention of many researchers because their peculiar properties, namely high surface area, tunable pore sizes and surface chemical reactivity, make them suitable for many technological applications [3-4].

Since inorganic porous materials can be obtained in several forms and shapes (i.e., nanostructured particles, bulky monoliths/aerogels, nanowires, thin films/coatings), many studies are focused on the production of oxides, mainly silica [5-8], titania [9-10], anodic alumina and composites [11-12]), as well as other ceramics, such as natural and/or artificial modified clays, zeolites (leader products in the microporous range) [13], silicon wafers [14-15], metal carbides and nitrides [16-19]. In recent years, the synthesis of thin porous oxidic/ceramic films [20-21] has received a great attention, especially in the field of membrane science and technology. For instance, composite asymmetric membranes consisting of macroporous substrates and thin micro- and mesoporous films have been developed to fabricate devices which can be used for the separation of chemicals, but also for more sensitive applications, such as dosing of chemicals in drug-delivery systems, microfluidics and Lab-on-a-chip devices, sensors, catalytic substrates and many others [22-24]. Furthermore oxidic/ceramic coatings with a well organized porosity are of interest for developing devices which can be exploited in advanced environmental applications. As reported by Franzoso *et al.* [25], one of the main issues to be solved nowadays is to fulfill the always increasing demand of fresh water by human population. Since the continental rainfall cannot sustain the demand of water, remediation processes of contaminated water are becoming more and more important [26]. In this context, the possibility of using “smart” membranes (with a specific porosity/reactivity) to be exploited for the clarification and remediation of wastewater is attracting the attention of worldwide experts [27-28]. Another very interesting application of porous oxidic thin films is in dye-sensitized solar cells (DSSCs), which offer a very promising alternative for future energy supply [29]. This

technology requires a photo-anode, which is typically made by a layer of mesoporous titania deposited onto a conductive glass substrate. Since the electron diffusion in such layer depends also on the porosity of the system, a better control of these parameters (in particular on the way of deposition) is very important for optimizing their photovoltaic performances [30]. These few case studies highlight how the production of thin films with controlled porosity is becoming a topic very attractive not only for a specific field of research, but rather in a multidisciplinary viewpoint.

The sol-gel polymerization process represents a key procedure for the bottom-up synthesis of such systems, but often this process is not enough versatile to form stable pores of appropriate size, therefore it is necessary to resort to templating agents [31-32]. In this respect, molecular and/or polymeric amphiphiles (i.e., surfactant and/or block copolymers) can be employed not only to take advantage of their self-assembly into micelles with well-defined size and geometry, but also to exploit the spontaneous organization of micelles in ordered arrangements which act as structure driving agents (in the soft-templating procedure, *vide infra*) [33-34].

Another important key-factor in the preparation of these advanced porous materials is also the deposition technique selected, which can influence both the porous architecture of the solidified film and the coating thickness [21]. Among the several deposition techniques, spin-coating on appropriate substrates gave valuable results [35-36]. The peculiarity of spin-coating deposition, in fact, is the fast spin rate, which induces the almost complete elimination of extra-solvents and the freezing of the templated nanostructure, leaving a well-ordered network of nanosized domains that reflects the arrangement of the driving agents [37-38].

Given the variety of porous oxidic materials existing and the number of methods useful for inducing controlled-porosity, a discussion around them is mandatory. Moreover, in the literature, several reviews are focused on sol-gel [5,32,39], templating [9,40-41] or deposition techniques [42-44], but only few of them [5,45] consider these three aspects together. The following paragraphs are therefore devoted to the description of a possible route to follow for obtaining well-ordered inorganic porous oxides, focusing on the sol-gel chemistry, soft-templating, and spin-coating deposition processes, as in our opinion their combination constitutes the simplest and most effective route to achieve the purpose. With the aim of helping users in the field of highly-porous organized films, advantages and disadvantages of each synthetic step are deeply discussed and the relative critical points highlighted. Additionally, soft- and hard-templating synthetic procedures are discussed and compared.

2. Sol-gel chemistry

2.1 Historical and economical (contemporary market) summary

The term "sol-gel" was firstly coined by Graham *et al.* in 1864 [46]. In particular, Graham and collaborators observed that the hydrolysis of TetraEthyl OrthoSilicate (TEOS) under acidic conditions produced SiO₂ in the form of a "glass-like material" [39]. From that point, and continuing in the following years, several advances have been made by many researchers worldwide. In particular, an extensive step forward was done by the Mobil Oil Company in 1992 with the development of a siliceous material with a periodic porous structure, known as M41S, synthesized with the help of a surfactant as template [47-48]. This class of highly-ordered porous materials (with pores typically oriented in a cylindrical array) found applications mainly in catalysis. The use of such mesoporous materials with homogeneously distributed pores and high surface areas as catalytic substrates in oil refinery opened to their industrial and technological development. In the same years also the academy increased fundamental and applied research on sol-gel chemistry. Under this point of view the work published by Hench and co-worker in 1990 [39] is a milestone and can be considered the first important systematic study on the sol-gel chemistry and mechanisms. For a wide and well-detailed discussion around sol-gel chemistry historical achievements, authors suggest to carefully read the information contained in Ref. [5].

In addition, as reported by Ciriminna *et al.* [5], in the last 30 years there was a remarkable growing interest around sol-gel chemistry and, starting from the late 1980s, the sol-gel method has been

continuously and thoroughly investigated, becoming an important tool for the development of novel materials with applicability in several productive areas. Most of the interest around the sol-gel approach is due to its high potential impact on the market. Important advantages of sol-gel processes over conventional materials and technologies are the low synthesis temperatures and the high purity of final products, which are key aspects to reduce production costs of high-performance and functional materials.

The worldwide demand of the market concerning sol-gel products is estimated for \$ 2.2 billion in 2017 (in 2011 it was estimated to be \$ 1.4 billion), mostly for silica-based materials and liquid formulations (i.e., for nanocoatings) [5]. In fact, the foremost sol-gel applications are currently in the coatings industry. Relevant examples are anti-reflective glass for facades, museums display cases, showrooms, silicon solar cells, nonhazardous anti-corrosive sol-gel coatings to replace chromate conversion coatings, sol-gel optical coatings for TV screens and protective coatings in general. However new expanding applications have to be considered, for instance in the optical and opto-mechanical industry and in cosmetics. Besides those also biomedicine applications are expected to boost the market of sol-gel products. In fact nanocarriers for controlled drug delivery, made of siliceous regularly-mesoporous supports prepared via sol-gel techniques (and templated via soft templating), received special attention in recent years, since they are suitable tools for an efficient delivery of drugs or diagnostic agents to the target sites reducing at the same time the systemic drug toxicity and the adverse side effects to healthy tissues. Moreover, these carriers can be loaded with a relatively large variety of drug molecules (e.g., small molecules, peptides, nucleic acids) which are protected from cleavage by external agents [49].

Market data and forecasts confirm the rapidly growing interest in sol-gel processes and products, also witnessed by increasing efforts of companies in R&D and by the expansion of the number of providers of silica precursors. This trend clearly demonstrates that the sol-gel technique is a stimulating field of research able to attract large economical investments.

2.2 Sol-gel synthesis: Reactivity in different chemical environments

The sol-gel process involves polycondensation reactions of monomers into a colloidal solution (*sol*) which evolves into an integrated network (*gel*) of either nanoparticles or bulky polymerized networks [5,8]. Typical precursors of such kind of reactions are metal alkoxides or chloride salts, but also other types of precursors can be used [50-51]. Considering silica, the most frequently used silicon-containing precursors are branched alkoxides of the Si(OR)₄ type, in which OR designates alkoxide groups.

Usually alkyl moieties (-R) are methyl (-CH₃) or ethyl (-C₂H₅) groups, giving TetraMethyl OrthoSilicate (TMOS) or TEOS, respectively [52]. Beside them, also other alkoxide-derived precursors are used, including, for instance, sodium silicate solution or waterglass (Na₂SiO₃) [51,53].

Water is the most common solvent for sol-gel syntheses, however, especially for preparing mesoporous thin films and membranes, it is very convenient to carry out sol-gel reactions in non-aqueous media [54]. Inorganic precursors are generally dissolved in the organic solvent and hydrolyzed with stoichiometric quantities of water. Then, as solvent evaporates, polymerization of silicate species around the templating assembly continues until a solid hybrid nanostructure is obtained. The following reactions explain the simultaneous hydrolysis, condensation and polymerization reactions involving alkoxides, leading water and alcohol as secondary byproducts [55].



Hydrolysis mechanisms involve a nucleophilic attack of O lone pairs of H₂O molecule on the Si atoms [56]. Because of the polarized Si-O bonds, silicon atoms hold a partial positive electronic charge δ^+ , which determines the kinetics of the nucleophilic attack and, consequently, of the hydrolysis reaction. Generally, since both hydrolysis and polycondensation processes are rather slow due to the low polarity of the Si-O bond in the initial precursor (Si atom in TEOS bears a positive charge δ^+ of 0.32), a catalyst is required [5,8]. Hydrolysis and condensation steps of alkoxides are catalyzed either by bases, which carry strong negative charges (i.e., OH⁻), or by acids (i.e., H₃O⁺): in the two cases the reaction mechanism changes completely. A comparison between the two catalyzed reaction mechanisms is reported in **Figure 1** [57].

The structure of a sol-gel material evolves sequentially because it is the product of successive and/or simultaneous hydrolysis, condensation, and their reverse reactions (esterification and depolymerization, respectively) [58]. In details, silica polymeric textured gels are obtained if the hydrolysis rate is faster than the condensation step: this is usually achieved for acidic catalysts. In the literature, a large range of acids has been tested as useful catalysts, including HCl [59], HF [60], or carboxylic acids [61]. Vice versa, proton acceptors (bases) accelerate the condensation reactions more than hydrolysis; therefore, the formation of denser colloidal silica particles and/or colloidal gels is favored. Aqueous NH₃ is the most frequently used basic catalyst [62], but also Lewis bases are sometimes adopted [39].

Remarkable differences in particle size and porosity are also observed in the two cases (see for instance the schematic diagram of the silica film texture obtained via sol-gel in presence of acid or base catalyst reported in **Figure 2**) [63]. These differences can be easily explained by considering the different kinetics of silanols condensation, which occurs more rapidly in an acid medium, resulting in the formation of larger particles and well formed granules [64]. Thus, basing on what evidenced in **Figure 2**, in a sol-gel process the use of acid as catalyst allows the growing of a rather dense silica thin film/coating.

However, even though sol-gel is the simplest way for obtaining oxidic materials, there are several parameters which need to be considered (and monitored) during the synthesis to avoid undesired effects. Apart from the choice of the proper catalyst, as reported by Danks *et al.* [50], one of the main concerns related to the sol-gel process is the thermal treatment. In particular, during the sol-to-gel conversion, precursors require a heating step, which can be performed under either air or inert-gas atmosphere. Such thermal treatment is crucial for fixing the final desired architecture, although it can lead to a number of problems caused by a non-uniform and non-controlled heating, for instance possible reactions with the crucibles/containers and development of gaseous by-products [65]. Nevertheless, the cooling rate can also lead to a sintering phenomenon, causing a loss in terms of both surface area and porosity [50]. Another crucial point for sol-gel processes is the water content in the synthesis mixture, which can influence the hydrolysis/polycondensation reactions of precursors. This can be a factor limiting the use of alkoxides as precursors. For this reason, several studies are focused on non-hydrolitic sol-gel processes, where the hydrolysis reaction is replaced by direct condensation reactions with solvents (such as alcohols, ethers and ketones) [50,66].

3. Principles of templating and methods for inducing porosity

3.1 The importance of templating

As evidenced in the previous paragraph, the sol-gel process offers a very flexible approach for the synthesis of a wide range of materials [67]. However, even though sol-gel guarantees several advantages (such as a very high versatility in terms of composition and shape control, together with low-cost of processing), this chemical route cannot provide a significant control of the final microstructure (and porosity architecture) due to both shrinking and sintering phenomena occurring during the drying and cooling steps, respectively [50,68]. Thus, to introduce an accurate porosity control (in terms of both shape and size), a templating action is often strongly recommended. The first guiding principles in the synthesis of highly porous architectures in materials were developed in zeolite science [69-71]. As well introduced in Schüth's work [71], the principle behind

templating is to generate a porous system in the synthesized materials which is a negative replica of the selected templating agents. In this regard it is worth specifying that the higher the control in dimension and shape of the porous network, the higher the selectivity (for instance in membrane or in catalysis applications). Importantly, porosity dramatically influences the final density of the material and this is fundamental, for instance, in the preparation of light-weight substrates, such as in biomedicine. In several situations, both shape and size of the resulting porous system are directly and clearly correlated to the adopted porogens, but sometimes the role of the template remains unclear as for the case of microporous materials. Conversely, a more direct correlation between the templating agents and the porous solid is registered in the case of mesoporous materials, where a direct replication of the template is realized (see [71], and references within). Additionally, as reported by Bao and co-workers [69], template plays a key-role also in the synthesis of materials with particular architectures (as for hollow spheres).

Entering more in details in the templating approach, in order to structure a solid at the nanometer level the most widely used methods for inducing regular porosity and consequent high surface area are two: soft-templating (or endotemplating) and hard-templating (or exotemplating) [70-71].

Scheme 1 shows the main differences between the two templating procedures. Basically, these differences rely on the state of the matter of the templating agents and in the mechanism of formation of the desired porous architectures. In soft-templating, both porogens and sol-gel precursors are initially liquid phases. Subsequently, while precursors start the hardening process, soft-templates remain in the liquid state, leaving empty spaces within the solid (endo-templating). Conversely, in hard-templating, porogens are in the solid phase, whereas the sol-gel precursors are liquid and diffuse in the solid network before to gelify. Therefore, in this last case the principle of templating is exactly the opposite of the soft-templating one, since precursors start to solidify within the solid porogen (exo-templating). Both approaches present advantages and disadvantages, and different critical points that deserve a detailed and specific discussion (see the following paragraphs).

As the last templating strategy mentioned, we report the salt templating method, already known for the synthesis of macroporous polymers and carbon [72], and recently discovered to be suitable for the synthesis of oxidic materials. In this approach the properties of different cation/anion present in a salts solution are applied to direct the synthesis towards the formation of a porous network and/or towards the formation of an assembly of small particles creating an interparticle porosity [6]. This method presents to main advantage to avoid toxic and/or expensive reactants and to be environment friend since the salt used as porogen can be recovered and reused.

3.2 Soft-templating: Micellization, supramolecular architectures and controlled porosity

As summarized in both **Scheme 1** and **Scheme 2**, soft-templating is related to the formation in solution of supramolecular cooperative systems of amphiphilic surfactants or polymers and inorganic species [40,73].

Amphiphiles are particular molecules containing a hydrophilic part (head) and a hydrophobic chain (tail), which at certain conditions (i.e., when the surfactant concentration is greater than the critical micellar concentration or CMC) spontaneously aggregate forming supramolecular structures (i.e., micelles), as for membranes in living cellular organisms (i.e., the double layer of phospholipids). Since these colloidal aggregates are in equilibrium with the isolated species (amphiphilic molecules/macromolecules and ions) present in the solution, micelle formation (and stability) is concentration-dependent. These supramolecular aggregates (called hosts) can be classified into normal and reverse micelles, emulsions, vesicles or liquid crystal phases, forming spheres, rod-like short cylinders, lamellar sheets, worm-like structures and so on, which drive the growth of the structured material (called guest) [9,74-80]. The possible architectures shown by aggregation of amphiphilic molecules are reported in **Scheme 2** [73].

Obviously, the principles governing the aggregation of amphiphiles are beyond the aim of this review, although it suffices to know that solution thermodynamics, interfacial phenomena and hydrophilic/hydrophobic effects are at the basis of the supramolecular self-assembly of these molecules [81].

The most diffused amphiphiles used in soft-templating approaches are surfactants. As reported by Gulians *et al.* [42], the original M41S family of mesoporous molecular sieves was originally obtained in alkaline environment by using CTAB (a cationic surfactant) as structure directing agent. The discovery of SBA-type ordered mesoporous silica materials, having thick pore walls and large pores, synthesized under acidic conditions with the use of non-ionic PEO-PPO-PEO triblock copolymers (i.e., Pluronic P123 and F127) as soft-templates, is an important milestone in this context [82-83]. The use of the Pluronic family as soft-templating agents has been widely investigated and there are several studies of their use for the synthesis of inorganic thin films [84-87]. As reported in **Figure 3**, the most common ordered mesoporous structure obtained is the two dimensional hexagonal phase generated by close-packed hexagonal arrays of cylindrical micelles [88]. Moreover, the bi-continuous cubic gyroid phase is very attractive for applications requiring a size-selective diffusion and/or transport of chemicals.

In addition to the Pluronics, another very promising PEO-containing block-copolymer used for the production of mesoporous inorganic films is poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PEO) [89-90]. For example, Yu *et al.* [91-92] reported the synthesis of mesoporous silica films obtained by using two different block-copolymers of the PS-*b*-PEO family, namely PS₂₁₅-*b*-PEO₁₀₀ and PS₃₅-*b*-PEO₁₀₉. Solvent evaporation-induced self-assembly (EISA) was used as deposition technique and syntheses were carried out by TEOS polymerization in 2 wt.% THF/water in the presence of HCl as acid catalyst. Transmission electron microscopy (TEM) micrographs of calcined silica films prepared with a volume ratio of silica/block-copolymer 60/40 are reported in **Figure 4**, showing the presence of cubic close-packed spherical *Pm3n* porous phase. Moreover, authors reported that the pore size increases together with the block-copolymer molecular weight, thus pore size can be rationally modulated by choosing the appropriate template.

In another case study, Deng and co-authors [93] reported the use of PS₁₂₅-*b*-PEO₂₃₀ for the production of ordered large mesoporous carbons (pore size ca. 23-26 nm) and silica (ca. 30 nm), with highly-ordered spherical large mesopores organized in a cubic (*fcc*) symmetry.

Moreover, mesoporous silica films with different pore morphologies (as shown in **Figure 5**) were obtained by spin-coating mixed micellar solutions containing TEOS as inorganic precursor, PS-*b*-PEO copolymers as organic structure-directing agents, benzene and ethanol as solvents, and HCl as sol-gel acid catalyst [94]. Samples with the highest TEOS/block-copolymer weight ratio (95/5) present stacked spherical large-mesopores, homogeneous in size. Experimental evidences allowed concluding that pores size is influenced by the PS/PEO ratio and that it is possible to predict the diameters of the porous system varying the size of the copolymer blocks [95]. Reducing the TEOS/block copolymer weight ratio to 90/10, and consequently decreasing the hydrophilic/hydrophobic solvent ratio, the mixed micellar solution becomes more hydrophobic and PS-*b*-PEO chains self-assemble in a supramolecular system arranged around a line instead of a dot: this way a minimization of the surface free energy is obtained, forming worm-like structures. By continuing reducing the TEOS/block-copolymer weight ratio, the colloidal system approaches the conditions for reverse micellization. Since reverse micelles work as nanoreactors, they are able to produce silica particles with an average diameter (in the reported case) of ca. 25-30 nm.

The use of high-molecular weight PS-*b*-PEO as soft-templating agents was also investigated for the production of stacked spherical porous systems made by titania, obtaining porosity of ca. 40, 60 and 100 nm by using PS₃₈₅-*b*-PEO₁₂₀₅, PS₅₆₃-*b*-PEO₁₆₁₄, and PS₉₆₂-*b*-PEO₃₄₀₉ as templates, respectively (as reported in **Figure 6**) [96].

Interestingly, by taking advantage of the supramolecular assembly of amphiphiles, hybrid materials can be produced by combining amphiphilic block-copolymers, like poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO), with metal oxides (i.e., TiO₂ and Nb₂O₅), which selectively swell the

hydrophilic PEO block of the block copolymer [97]. The PEO-block can be easily decomposed by heating under inert atmosphere, whereas the PI-block, which contains two sp² carbons per monomer unit, is converted into a solid amorphous carbon coating acting as a rigid and thermally stable support for building the mesostructured oxidic walls, thus preventing the collapse of the oxide structure at temperatures higher than 550-600°C [98-99]. **Figure 7** shows titania and niobia samples before and after the thermal treatments under air or argon atmosphere: the resulting materials possess hexagonally ordered porous architectures characterized by higher crystallinity rather than materials grown at lower temperatures in the presence of other block-copolymers as structure directing agents [100-101].

3.3 Hard-templating

The hard-templating approach (also named nanocasting) refers to the use of hard materials (mostly inorganics such as anodic alumina or porous silica, but also polymeric latex particles) as structure directing agents [102]. The principle behind this procedure is that liquid precursors in solution are percolated inside the voids of the solid templating system and polymerized in situ, thus hard-templates simply behave as scaffolds around which the desired material is forcedly grown (from here the term “exo-templating”) [71]. Once the growing material reaches the desired morphology, hard-templates are removed either by selective wet treatments or calcination (the two routes are typically used for either inorganic or organic solid porogens, respectively), thus leaving a final material with pores which are a perfect negative replica of the hard-templates used (**Scheme 1**) [9].

The structural order in the synthesized materials is obtained more easily by using hard-templating scaffolds than in the previously discussed soft-templating approach, where the templating action is realized at the liquid level. Key steps in the nanocasting procedure are the choice of the best method for precursor deposition (the growing layer must be as homogeneous as possible), the template removal (to avoid the collapse of the entire nanostructure or even its chemical modification) [40], and the interaction between the precursor (guest) and the surface of the mesoporous host, which affects the host soaking realized by the guest. In particular considering this last critical point, if the guest-host interaction is too weak, the loading of the precursor is not complete and this produces disordered nanostructures. The use of silica molds tend to prevent this issue since surface silanol groups of the mold ($\equiv\text{Si-OH}$) can attract polar guest molecules forming hydrogen bonds or favoring chelation-based interactions towards metal ions of the guest precursors [103-105].

There are several different approaches to the hard-templating technique, as summarized by Zhao and co-workers in Ref. [9], which also depend on the nature of the template and of the nanomaterials that are synthesized. In addition to metal oxides, also metal sulfides, semiconductors, metals and polymers have been synthesized in the form of nanostructured materials or nano-objects by hard-templating methods [106-107]. Similarly, mesoporous silica, and also porous alumina and polymer membranes have been used as hosts in nanocasting procedures.

As reported by Stein [45] and Velev *et al.* [108], periodic porous silica can be prepared using TEOS to fill the voids between polymer particles (PS latex sphere) in colloidal suspension. In detail, in these syntheses, either pure alkoxides [45] or alkoxides in presence of surfactants [108] were used. In both cases the selected alkoxide is able to condense between the polymeric spheres within several hours. After thermal treatment under air atmosphere (i.e., calcination), necessary to remove PS spheres, amorphous mesoporous silica with pore diameters ranging from 2 to 40 nm depending on the diameter of the starting hard-templates were obtained. The entire hard-templating procedure was summarized in **Figure 8**. Furthermore, the pore size distribution can be further tuned in the presence of surfactants. In this dual-templating synthesis (where the term “dual” refers to the use of both soft- and hard-templates), the TEOS/surfactant mixture was initially percolated through the hard-templates, and subsequently solidified by condensation reactions. After removal of both templates by calcination, the final material presents a bimodal porous architecture with macropores (few hundreds of nanometers) due to the original PS spheres, and mesopores (minor than 4 nm)

[45,108]. The surface area of the product thus obtained was significantly higher than the one obtained from pure TEOS (1340 vs. ca. 200 m²g⁻¹).

Quite recently, a significant study concerning the production of highly porous oxides and metals by using the hard-templating approach has been published [109]. In detail, hierarchical porous silica with a bi-continuous pore structure were used as hard-templating agents for preparing Co₃O₄, NiO, as well as cobalt, nickel and silver metal monoliths. The process adopted is very simple and it consists in three steps: i) impregnation of the silica monoliths (hard-templates) with aqueous solutions containing Co, Ni, and Ag salts, ii) thermal treatments carried out either under nitrogen or under air atmosphere depending on whether the final desired materials should be metals or oxides, and iii) removal of the silica hard-templates by simply washing with a 3M KOH solution.

Furthermore, the hard-templating procedure is also suitable for inducing chiral behaviors in the prepared materials, as in the case of titania films synthesized by using chiral nematic mesoporous silica films as hard-template, reported in Ref. [110]. Even here, the process adopted is a three steps procedure: i) impregnation of the silica nematic films by aqueous TiCl₄ solution, ii) annealing in a furnace at 600°C to obtain the crystalline Ti-oxide, and iii) removal of the silica hard-templates by washing with 2M NaOH. Structural features of the chiral nematic silica template ranging from the mesoscopic to macroscopic size regimes are retained in the final product, resulting in mesoporous TiO₂ films that reflect the circularly polarized light. This way, it is possible to obtain highly porous titania with a well-ordered architecture that can be exploited in different applications, such as photo-catalysis or sensing. Moreover, this particular hard-templating approach opened the possibility to produce different oxidic materials with a very precise chiral nematic organization, extremely difficult to obtain by using other templating methods.

3.4 Soft- vs hard-templating: A critical comparison

Although soft- and hard-templating approaches are widely diffused, both techniques still present problems and disadvantages, the most important reported in the following and summarized in **Table 1**.

1. The main critical step for both procedures is the template removal, because of the high-risk of deformation and/or collapse of the nanostructures [40], in particular with soft-templating agents which act in the liquid phase.
2. In general, for materials produced via soft-templating and/or hard-templating by using polymer latex particles as driving structures, it is necessary to perform the sol-gel synthesis at relatively low temperature in order to avoid the porogen degradation prior than the formation of a stable porous architecture. This limit is also reflected in the structural organization of porous materials, which are generally amorphous [97,100-101].
3. Depending on the types of amphiphiles selected, soft-templates can be removed by thermal treatments, which sometimes lead to the formation of carbonaceous residues difficult to remove from the material surface or even entrapped in the sintered solid [102,111].
4. With hard-templating, problems due to structural restrictions and compatibility of mold and templated materials have to be considered. In particular, a rigid mold could produce some undesirable voids or cracks generated by the rigid structure of the hard-template, which not always follows the forming material [112].
5. The removal of hard-templates is difficult, the entire procedures are quite complex and involve several steps, often requiring hazardous chemicals (for instance HF or strong base solutions, for the dissolution of siliceous molds) which can be also responsible of the chemical modification of the precursor and/or of the final material [112-113].

The applied research focused on the development of both novel and potentially-useful techniques to induce controlled porosity on materials is still continuing. Worldwide researchers are involved in an attempt to better the already existing templating methods, pointing toward a finer control of the processes also according to green chemistry commandments.

In fact, basing on concepts here resumed, both procedures (i.e., soft- and hard-templating) require non-environmental friendly and sometimes non-trivial treatments. On the other hand, as extensively discussed throughout the manuscript, once experimental difficulties are overcome, both methods allow obtaining extremely highly-ordered nanostructures in the final product, thus justifying their use.

Additionally, by making a comparison between advantages and disadvantages of both techniques, the soft-templating approach seems to be the more versatile *modus operandi* since different regular morphologies can be easily reached and maintained. However, in our opinion, the deposition techniques used are fundamental for achieving the desired hierarchically ordered porous thin films/coatings.

4. Deposition techniques for the production of inorganic thin films/coatings: The spin-coating case study

Since mesoporous inorganic materials are rigid solids and as such cannot be easily shaped as thin films/coatings at the post-synthesis level, the reactive sol-gel mixture has to be deposited as a thin film, or the synthesis conditions should favor the formation of a thin interfacial layer [43]. In this context, a distinction between the different kinds of porous organization is mandatory. In fact, for instance membranes for microfluidics can be classified as screen-filters or depth-filters (**Scheme 3**) [114]. Screen-filters are well-ordered vertically aligned straight-through pores devices and their separation principle is based on the sieving mechanism: all particles bigger than the pore diameter are retained, whereas smaller ones can pass through the pores. Vice versa, depth-filter systems are characterized by having a tortuous disordered porous network and their separation principle is based not only on the sieving mechanism, but also on the interaction between the bulky part of the filter and chemicals.

As reported by Pevzner *et al.* [43], conventional methods for the production of thin films are spin-coating and dip-coating deposition. In both methods the liquid solution (containing inorganic precursors, solvents, polymerization catalysts and templating agents) is directly deposited onto the support. Among other techniques, spin-coating is the most easily-applicable one for obtaining uniform thin layers on flat surfaces [115-116]. Experimentally, a small amount of the coating material is deposited onto the center of the support. Subsequently, the support is rotated at high speed in order to spread the coating material by the centrifugal force. In general, the higher the rotations speed, the thinner the film [117-118]. Therefore, by selecting the appropriate spin rate, it is possible to modulate the film thickness [118].

The production of thin films by spin-coating was initially reported by Ogawa in the 1996 [119]. Recently, Garcia Juez *et al.* [22] reported a methodology for the preparation of self-standing 100-200 nm thick mesoporous silica membrane interconnects. In particular, as stated by the authors, interconnects may become an important component in future microfluidic device technology since they allow the extension of microfluidic architectures into the third dimension. By spin-coating of a sol-gel solution containing TEOS (the silica precursor) and CTAB as soft-templating agent, authors produced functional thin layers/coatings made by mesoporous silica deposited onto commercial Si_3N_4 macroporous (diameter of 500 nm) support. The adopted procedure is as follows: i) to avoid penetration of the silica sol in the underlying macroporous level, perforations of the supports were filled by spin-coating deposition of a PMMA solution to generate a film, ii) spin-coating deposition of the silica sol, iii) overnight drying of the silica sol to generate a silica coating, iv) PMMA removal by solvent washing, v) annealing at 600 °C for 2 hours in air. **Figure 9** shows the morphology of the silica coating, evidencing both the film homogeneity and self-standing property. A different approach was also proposed [72] for the production of a mesoporous silica film obtained by spin-coating deposition of silica nanoparticles (obtained by using block-copolymers as soft-templates) onto a similar macroporous support. This way, the tortuous and disordered voids comprised between the silica nanoparticles generate a depth-filter membrane which can be applied to control the transport of chemicals (for instance, dyes or proteins) in aqueous environment.

Another procedure for the production of silica films by spin-coating deposition of a sol-gel solution containing TEOS in the presence of PVP (i.e., poly-vinylpyrrolidone) as organic porogen was proposed by Toniutti *et al.* [36]. They followed the increase of pore size (i.e., in the microporous range) due to thermal treatments, establishing the best temperature condition to reach the maximum porosity. This formulation was subsequently deposited on mesoporous supports to evidence molecular sieving capacities.

In general, the use of spin-coating for the deposition of inorganic functional thin layers/coatings is common in many fields, starting from microfluidics for molecular separation (membrane), detection (sensing) and dosing to lab-on-a-chip systems and others.

Beside the very interesting results obtained and the very good performances of this simple deposition technique, spin-coating possesses some drawbacks in particular concerning the size and shape of the substrates. In fact, as reported by [120], large supports are difficult to be homogeneously deposited by this method. Additionally, in a typical spin-coating deposition, minor than the 5% of the starting solution is deposited successfully onto the substrate forming the thin film, whereas the complement percentage is lost due to the rotation of the spinner. Lastly, the final morphology of the sample can be influenced by several parameters (such as spin speed, time of spin, acceleration, fume exhaust, etc...) [121]. Surely, all these parameters can be modulated in order to obtain the desired morphology of the layers, but, on the other hand, all these factors can really complicate the deposition procedure.

5. Outlook and perspectives

Starting from the examples already offered by nature (i.e., natural zeolites, animal and human bones, marine corals and diatoms, etc...), men began to produce ordered porous materials, passing from the macro- to the meso- and microporous level. In the past years, tailored porous inorganic materials have become of interest in many technologic fields. The peculiar properties of these materials, related to the hierarchically-induced porosity, allow their use as membranes for selective separation, in microfluidics, or in electronics. Recently, together with the increase of attention to environment safeguarding and green chemistry, other possible applications have emerged for highly porous thin films, like energetic materials for fuel cells and hydrogen conversion or porous photocatalytic materials for wastewater treatments (necessary for the reductions of human-based pollutants). In this respect, the synthesis of new high-surface area and highly-ordered porous materials/coating is expected to significantly increase.

With this review we would like to present a possible route to follow for the simple preparation of inorganic porous thin layers/coatings, providing a precise discussion around the chemical principles behind sol-gel chemistry, templating procedures, and spin-coating deposition.

6. Acknowledgements

This work was realized with the financial support for academic interchange by the Marie Skłodowska-Curie Research and Innovation Staff Exchange project funded by the European Commission H2020-MSCA-RISE-2014 within the framework of the research project Mat4treaT (Project number: 645551). Compagnia di San Paolo and University of Torino are gratefully acknowledged for funding Project Torino_call2014_L2_126 through “Bando per il finanziamento di progetti di ricerca di Ateneo – anno 2014” (Project acronym: Microbusters).

References

- [1] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, **Pure and Applied Chemistry** 57 (1985) 603-619.
- [2] A. Taguchi, F. Schüth, **Microporous and Mesoporous Materials** 77 (2005) 1-45.
- [3] A.-H. Lu, F. Schüth, **Advanced Materials** 18 (2006) 1793-1805.
- [4] A. Budnyk, A. Damin, S. Bordiga, A. Zecchina, **Journal of Physical Chemistry C** 116 (2012) 10064-10072.

- [5] R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L.M. Ilharco, M. Pagliaro, **Chemical Reviews** 113 (2013) 6592-6620.
- [6] R. Nisticò, G. Magnacca, M. Antonietti, N. Fechler, **Zeitschrift für Anorganische und Allgemeine Chemie** 640 (2014) 582-587.
- [7] R. Nisticò, G. Magnacca, M. Antonietti, N. Fechler, **Advances Porous Materials** 2 (2014) 37-41.
- [8] C.J. Brinker, G.W. Scherer, *Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, CA (1990).
- [9] Y. Wan, H. Yang, D.Y. Zhao, **Accounts of Chemical Research** 39 (2006) 423-432.
- [10] A.C. Pierre, G.M. Pajonk, **Chemical Reviews** 102 (2002) 4243-4265.
- [11] Q.S. Huo, D.I. Margolese, U. Ciesla, P.Y. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schüth, G.D. Stucky, **Nature** 368 (1994) 317-321.
- [12] P.D. Yang, D.Y. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, **Nature** 396 (1998) 152-155.
- [13] A. Corma, **Chemical Reviews** 95 (1995) 559-614.
- [14] T. Sun, W. Mong Sang, W.-T. Park, **Applied Surface Science** 292 (2014) 843-851.
- [15] M. Li, M. Hu, Q. Liu, S. Ma, P. Sun, **Applied Surface Science** 268 (2013) 188-194.
- [16] A. Keffous, N. Gabouze, A. Cheriet, Y. Belkacem, A. Boukezzata, **Applied Surface Science** 256 (2010) 5629-5639.
- [17] K.-H. Lee, S.-K. Lee, K.-S. Jeon, **Applied Surface Science** 255 (2009) 4414-4420.
- [18] K. Bodišová, M. Kašiarová, M. Domanická, M. Hnatko, Z. Lenčėš, Z. Varchulová Nováková, J. Vojtaššák, S. Gromošová, P. Šajgalík, **Ceramics International** 39 (2013) 8355-8362.
- [19] M. Maleki, A. Beitollahi, J. Javadpour, N. Yahya, **Ceramics International** 41 (2015) 3806-3813.
- [20] Z. Chen, X. Wang, N. Brandon, A. Atkinson, **Journal of the European Ceramic Society** 37 (2017) 1031-1038.
- [21] C.G. Granqvist, **Solar Energy Materials and Solar Cells** 99 (2012) 1-13.
- [22] R. Garcia Juez, V. Boffa, D.H.A. Blank, J.E. ten Elshof, **Journal of Membrane Science** 323 (2008) 347-351.
- [23] M. Bueno Serrano, C. Despas, G. Herzog, A. Walcarius, **Electrochemistry Communications** 52 (2015) 34-36.
- [24] A. Bearzotti, J. Mio Bertolo, P. Innocenzi, P. Falcaro, E. Traversa, **Sensors and Actuators B: Chemical** 1-3 (2003) 107-110.
- [25] F. Franzoso, R. Nisticò, F. Cesano, I. Corazzari, F. Turci, D. Scarano, A. Bianco Prevot, G. Magnacca, L. Carlos, D.O. Martire, **Chemical Engineering Journal** 310 (2017) 307-316.
- [26] A.K. Kivaisi, **Ecological Engineering** 16 (2001) 545-560.
- [27] X. Li, A. Sotto, J. Li, B. Van der Bruggen, **Journal of Membrane Science** 524 (2017) 502-528.
- [28] A. Farsi, C. Malvache, O. De Bartolis, G. Magnacca, P.K. Kristensen, M.L. Christensen, V. Boffa, **Microporous and Mesoporous Materials** 237 (2017) 117-126.
- [29] J. Gong, K. Sumathy, Q. Qiao, Z. Zhou, **Renewable and Sustainable Energy Reviews** 68 (2017) 234-246.
- [30] N. Tasic, Z.M. Stanojevic, Z. Brankovic, U. Lacnjevac, V. Ribic, M. Zunic, T. Novakovic, M. Podlogar, G. Brankovic, **Electrochimica Acta** 210 (2016) 606-614.
- [31] N.K. Raman, M.T. Anderson, C.J. Brinker, **Chemistry of Materials** 8 (1996) 1682-1701.
- [32] G.J. de A.A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, **Chemical Reviews** 102 (2002) 4093-4138.
- [33] S.A. Jenekhe, X.L. Chen, **Science** 283 (1999) 372-375.
- [34] M. Lazzari, M.A. Lopez-Quintela, **Advanced Materials** 15 (2003) 1583-1594.
- [35] S. Barma, B. Mandal, **Microporous and Mesoporous Materials** 210 (2015) 10-19.

- [36] L. Toniutti, S. Mariazzi, N. Patel, R. Checchetto, A. Miotello, R.S. Brusa, **Applied Surface Science** 255 (2008) 170-173.
- [37] M. Lazzari, M.A. Lopez-Quintela, **Macromolecular Rapid Communications** 30 (2009) 1785-1791.
- [38] J.M. Gomez-Vega, M. Iyoshi, K.Y. Kim, A. Hozumi, H. Sugimura, O. Takai, **Thin Solid Films** 398-399 (2001) 615-620.
- [39] L.L. Hench, J.K. West, **Chemical Reviews** 90 (1990) 33-72.
- [40] Q. Zhang, W. Wang, J. Goebi, Y. Yin, **Nano Today** 4 (2009) 494-507.
- [41] Y. Liu, J. Goebel, Y. Yin, **Chemical Society Reviews** 42 (2013) 2610-2653.
- [42] V.V. Gulians, M.A. Carreon, Y.S. Lin, **Journal of Membrane Science** 235 (2004) 53-72.
- [43] S. Pevzner, O. Regev, R. Yerushalmi-Rozen, **Current Opinion in Colloid and Interface Science** 4 (2004) 420-427.
- [44] D.B. Hall, P. Underhill, J.M. Torkelson, **Polymer Engineering and Science** 38 (1998) 2039-2045
- [45] A. Stein, **Microporous and Mesoporous Materials** 44-45 (2001) 227-239.
- [46] T. Graham, **Journal of the Chemical Society** 17 (1864) 318-327.
- [47] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, **Nature** 359 (1992) 710-712.
- [48] 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, J.L. Schlenker, **Journal of the American Chemical Society** 114 (1992) 10834-10843.
- [49] M. Costanzo, F. Carton, A. Marengo, G. Berlier, B. Stella, S. Arpicco, M. Malatesta, **European Journal of Hystochemistry** 60 (2016) 2640.
- [50] A.E. Danks, S.R. Hall, Z. Schnepp, **Materials Horizons** 3 (2016) 91-112.
- [51] A.C. Pierre, A. Rigacci, SiO₂ aerogels, In: M.A. Aegerter, A. Rigacci (Eds.), **Aerogels Handbook, Advances in Sol-Gel Derived Materials and Technologies**, Springer Science, New York (USA), 2011, pp. 21-45.
- [52] K. Nakanishi, H. Minakuchi, N. Soga, N. Tanaka, **Journal of Sol-Gel Science and Technology** 13 (1998) 163-169.
- [53] A. Venkateswara Rao, A. Parvathy Rao, M.M. Kulkarni, **Journal of Non-Crystalline Solids** 350 (2004) 224-229.
- [54] Y. Wan, D. Zhao, **Chemical Reviews** 107 (2007) 2821-2860.
- [55] M.A. Aegerter, N. Leventis, M.M. Koebel, **Aerogels Handbook, Advances in Sol-Gel Derived Materials and Technologies**, Springer, New York, NY (USA), 2011.
- [56] J. Livage, M. Henry, C. Sanchez, **Progress in Solid State Chemistry** 18 (1988) 259-341.
- [57] J.E. Lofgreen, G.A. Ozin, **Chemical Society Reviews** 43 (2014) 911-933.
- [58] L. Duffours, T. Woignier, J. Phalippou, **Journal of Non-Crystalline Solids** 186 (1995) 321-327.
- [59] B. Zhou, J. Shen, W. Yuehua, G. Wu, X. Ni, **Materials Science and Engineering C** 27 (2007) 1291-1294.
- [60] M. Moner-Girona, A. Roig, E. Molins, **Journal of Sol-Gel Science and Technology** 26 (2003) 645-649.
- [61] P. Mezza, J. Phalippou, R. Sempere, **Journal of Non-Crystalline Solids** 243 (1999) 75-79.
- [62] C.R. Silva, C. Airoidi, **Journal of Colloid and Interface Science** 195 (1997) 381-387.
- [63] Y. Xiao, J. Shen, Z. Xie, B. Zhou, G. Wu, **Journal of Materials Science and Technology** 23 (2007) 504-508.
- [64] J.L. Gurav, I-K. Jung, H.-H. Park, E.S. Kang, D.Y. Nadargi, **Journal of Nanomaterials** (2010), Article ID 409310.
- [65] H.J. Kitchen, S.R. Vallance, J.L. Kennedy, N. Tapia-Ruiz, L. Carassiti, A. Harrison, A.G. Whittaker, T. D. Drysdale, S.W. Kingman, D.H. Gregory, **Chemical Reviews** 114 (2014) 1170-1206.
- [66] D.P. Debecker, P.H. Mutin, **Chemical Society Reviews** 41 (2012) 3624-3650.

- [67] G.J. Owens, R.K. Singh, F. Foroutan, M. Alqaysi, C.M. Han, C. Mahapatra, H.W. Kim, **Progress in Materials Science** 77 (2016) 1-79.
- [68] S. Sakka, **Handbook of Sol-Gel Science and Technology, Processing, Characterization and Applications**, Second Edition, Vol. 3, Kluwer Academic Publisher, Norwell (USA), 2005.
- [69] Y. Bao, C. Shi, T. Wang, X. Li, J. Ma, **Microporous and Mesoporous Materials** 227 (2016) 121-136.
- [70] I. Nowak, M. Jaroniec, **Topics in Catalysis** 49 (2008) 193-203.
- [71] F. Schüth, **Angewandte Chemie International Edition** 42 (2003) 3604-3622.
- [72] X. Liu, N. Fechler, M. Antonietti, **Chemical Society Reviews** 42 (2013) 8237-8265.
- [73] R. Nisticò, P. Avetta, P. Calza, D. Fabbri, G. Magnacca, D. Scarlone, **Beilstein Journal of Nanotechnology** 6 (2015) 2105-2112.
- [74] K. Yu, A. Eisenberg, **Macromolecules** 31 (1998) 3509-3518.
- [75] G. Landazuri, W. Fernandez, J.F. Soltero, Y. Rharbi, **Journal of Physical Chemistry B** 116 (2012) 11720-11727.
- [76] C. Sinico, A.M. Fadda, **Expert Opinion on Drug Delivery** 6 (2009) 813-825.
- [77] Z. Chu, C.A. Dreiss, Y. Feng, **Chemical Society Reviews** 7 (2013) 7174-7203.
- [78] P. Khullar, V. Singh, A. Mahal, H. Kumar, G. Kaur, M.S. Bakshi, **Journal of Physical Chemistry B** 117 (2013) 3028-3039.
- [79] L.K. Shrestha, R.G. Shrestha, N. Vilanova, C. Rodríguez-Abreu, K. Ariga, **Journal of Nanoscience and Nanotechnology** 14 (2014) 2238-44.
- [80] Y. Lee, J. Lee, C.J. Bae, J.-G. Park, H.-J. Noh, J.-H. Park, T. Hyeon, **Advanced Functional Materials** 15 (2005) 503-509.
- [81] G. Riess, **Progress in Polymer Science** 28 (2003) 1107-1170.
- [82] N. Pal, A. Bhaumik, **Advances in Colloids and Interface Science** 189-190 (2013) 21-41.
- [83] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, **Science** 279 (1998) 548-552.
- [84] O. Muraza, E.V. Rebrov, T. Khimiyak, B.F.G. Johnson, P.J. Kooyman, U. Lafont, M.H.J.M. de Croon, J.C. Schouten, **Chemical Engineering Journal** 135 (2008) S99-S103.
- [85] A.J. Kessman, E.E. DeFusco, A.W. Hoover, K.A. Sierros, D.R. Cairns, **Thin Solid Films** 520 (2012) 3896-3903.
- [86] X. Collard, B. van der Schueren, J.C. Rooke, C. Aprile, B.-L. Su, **Journal of Colloids and Interface Science** 401 (2013) 23-33.
- [87] I. Recloux, M. Mouanga, M.-E. Druart, Y. Paint, M.-G. Olivier, **Applied Surface Science** 346 (2015) 124-133.
- [88] M.-Y. Cheng, C.-J. Pan, B.-J. Hwang, **Journal of Materials Chemistry** 19 (2009) 5193-5200.
- [89] C.G. Goltner, S. Henke, M.C. Weissenberger, M. Antonietti, **Angewandte Chemie International Edition** 37 (1998) 613-616.
- [90] B. Smarsly, M. Antonietti, **European Journal of Inorganic Chemistry** 2006 (2006) 1111-1119.
- [91] K. Yu, A.J. Hurd, A. Eisenberg, C.J. Brinker, **Langmuir** 17 (2001) 7961-7965.
- [92] K. Yu, B. Smarsly, C.J. Brinker, **Advanced Functional Materials** 13 (2003) 47-52.
- [93] Y. Deng, T. Yu, Y. Wan, Y. Shi, Y. Meng, D. Gu, L. Zhang, Y. Huang, C. Liu, X. Wu, D. Zhao, **Journal of the American Chemical Society** 129 (2007) 1690-1697.
- [94] R. Nisticò, D. Scarlone, G. Magnacca, **Microporous and Mesoporous Materials** 190 (2014) 208-214.
- [95] R. Nisticò, G. Magnacca, S.A. Jadhav, D. Scarlone, **Beilstein Journal of Nanotechnology** 7 (2016) 1454-1460.
- [96] D. Chandra, T. Ohji, K. Kato, T. Kimura, **Physical Chemistry Chemical Physics** 13 (2011) 12529-12535.
- [97] J. Lee, M.C. Orilall, S.C. Warren, M. Kamperman, F.J. DiSalvo, U. Wiesner, **Nature Materials** 7 (2008) 222-228.

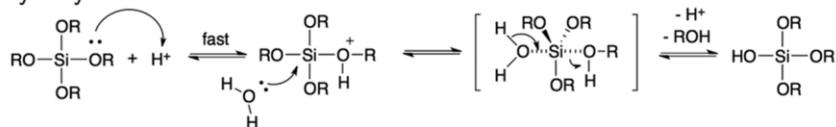
- [98] F. Zhang, Y. Yan, H. Yang, Y. Meng, C. Yu, B. Tu, D. Zhao, **Journal of Physical Chemistry B** 109 (2005) 8723-8732.
- [99] A. Venkateswara Rao, P.B. Wang, D. Haranath, P.P. Risbud, S.D. Kumbhare, **Ceramics International** 25 (1999) 505-509.
- [100] V.F. Stone Jr, R.J. Davis, **Chemistry of Materials** 10 (1998) 1468-1474.
- [101] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, **Chemistry of Materials** 11 (1999) 2813-2826.
- [102] A. Feinle, M.S. Elsaesser, N. Husing, **Chemical Society Reviews** 45 (2016) 3377-3399.
- [103] B.Z. Tian, X.Y. Liu, C.Z. Yu, F. Gao, Q. Luo, S.H. Xie, B. Tu, D.Y. Zhao, **Chemical Communications** 11 (2002) 1186-1187.
- [104] B.Z. Tian, X.Y. Liu, L.A. Solovyov, Z. Liu, H.F. Yang, Z.D. Zhang, S.H. Xie, F.Q. Zhang, B. Tu, C.Z. Yu, O. Terasaki, D.Y. Zhao, **Journal of the American Chemical Society** 126 (2004) 865-875.
- [105] B.Z. Tian, X.Y. Liu, H.F. Yang, S.H. Xie, C.Z. Yu, B. Tu, D.Y. Zhao, **Advanced Materials** 15 (2003) 1370-1374.
- [106] C.R. Martin, **Science** 266 (1994) 1961-1966.
- [107] H.F. Yang, D.Y. Zhao, **Journal of Materials Chemistry** 15 (2005) 1217-1231.
- [108] O.D. Velez, T.A. Jede, R.F. Lobo, A.M. Lenhoff, **Chemistry of Materials** 10 (1998) 3597-3602.
- [109] F.M. Sayler, A.J. Grano, J.-H. Smått, M. Lindén, M.G. Bakker, **Microporous and Mesoporous Materials** 184 (2014) 141-150.
- [110] K.E. Shopsowitz, A. Stahl, W.Y. Hamad, M.J. MacLachlan, **Angewandte Chemie International Edition** 51 (2012) 6886-6890.
- [111] Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, D. Zhao, **Chemistry of Materials** 18 (2006) 4447-4464.
- [112] A.-H. Lu, D. Zhao, Y. Wan, *Nanocasting: A Versatile Strategy for Creating Nanostructured Porous Materials*, RSC Nanoscience and Nanotechnology n° 11, RSC Publishing, Cambridge (UK), 2010.
- [113] R. Kumar, B. Chowdhury, The synthetic strategy for developing mesoporous materials through nanocasting route, In: *Advanced Functional Materials*, A. Tiwari, L. Uzun (Eds), John Wiley and Sons Inc, Hoboken (USA), 2015, pp. 59-128.
- [114] I.H. Huisman, Microfiltration. In: I.D. Wilson (Ed.), *Encyclopedia of Separation Science*, Academic Press, San Diego, CA (1990).
- [115] M. Ikawa, T. Yamada, H. Matsui, H. Minemawari, J. Tsutsumi, Y. Horii, M. Chikamatsu, R. Azumi, R. Kumar, T. Hasegawa, **Nature Communications** 3 (2012) 1176.
- [116] M. Hershcovitz, I.E. Klein, **Microelectronics Reliability** 33 (1993) 869-880.
- [117] F. Zhang, C. Di, N. Berdunov, Y. Hu, Y. Hu, X. Gao, Q. Meng, H. Siringhaus, D. Zhu, **Advanced Materials** 25 (2013) 1401-1407.
- [118] A. Uzum, K. Fukatsu, H. Kanda, Y. Kimura, K. Tanimoto, S. Yoshinaga, Y. Jiang, Y. Ishikawa, Y. Uraoka, S. Ito, **Nanoscale Research Letters** 9 (2014) 659.
- [119] M. Ogawa, **Chemical Communications** 10 (1996) 1149-1150.
- [120] M.D. Tyona, **Advances in Materials Research** 2 (2013) 195-208.
- [121] P.-C. Chang, J.G. Lu, **IEEE Transactions on Electron Devices** 11 (2008) 2877-2987.

Table 1. Critical steps relative to the templating procedure.

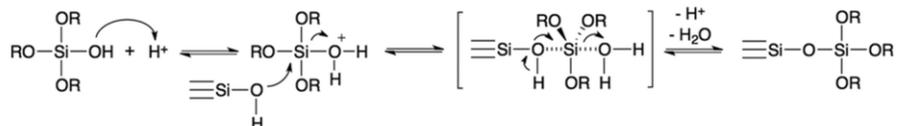
Critical steps	Soft-templating	Hard-templating (organic porogen)	Hard-templating (inorganic porogen)
Temperature of sol-gel process (host)	T < template degradation	T < template degradation	T < undesired modifications in molded host
Temperature of sol-gel process (guest)	More amorphous	More amorphous	More crystalline
Host-guest interaction	Easier since both host precursor and guest are miscible at the liquid phase	Risk of undesired voids/cracks due to structural restriction/compatibility between the rigid host and the liquid guest precursors	Risk of undesired voids/cracks due to structural restriction/compatibility between the rigid host and the liquid guest precursors
Removal of templates (host)	Thermal treatments can lead to undesired carbonaceous residues	Thermal treatments can lead to undesired carbonaceous residues	Use of hazardous chemicals (strong base or HF)
Removal of templates (guest)	Risk of deformation/collapse of the nanostructure	Risk of deformation/collapse of the nanostructure	Risk of deformation/collapse of the nanostructure

a) acid-catalyzed

hydrolysis

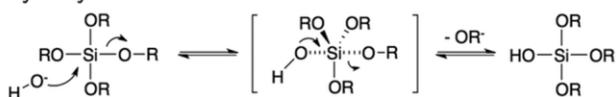


condensation



b) base-catalyzed

hydrolysis



condensation

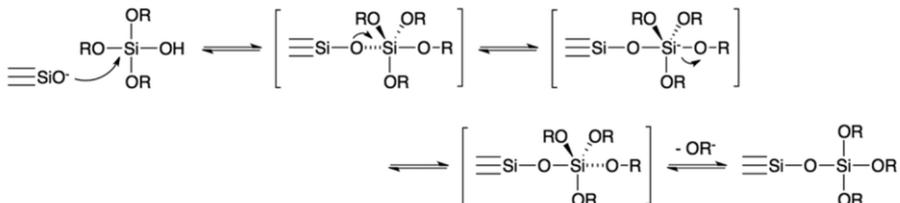


Figure 1. General mechanisms of hydrolysis and condensation of alkoxy silane precursors to form silica in (a) acid catalyzed conditions and (b) base catalyzed conditions. Condensation can produce either water or alcohol as a byproduct. Adapted and reproduced from Ref. [57] with permissions from the Royal Society of Chemistry.

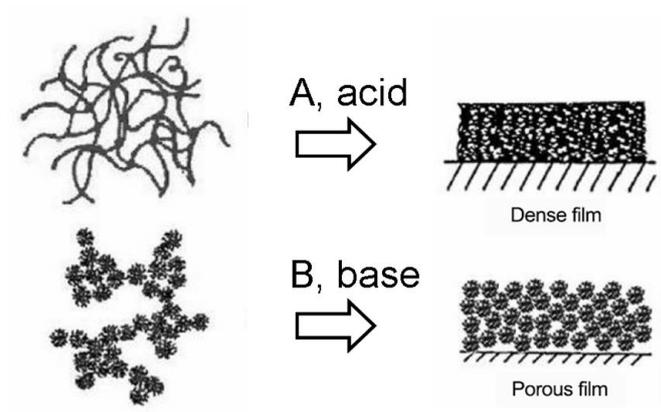


Figure 2. Schematic diagram of the formed network during sol-gel process with acid catalysis (A) and base catalysis (B). Adapted and reproduced from Ref. [63].

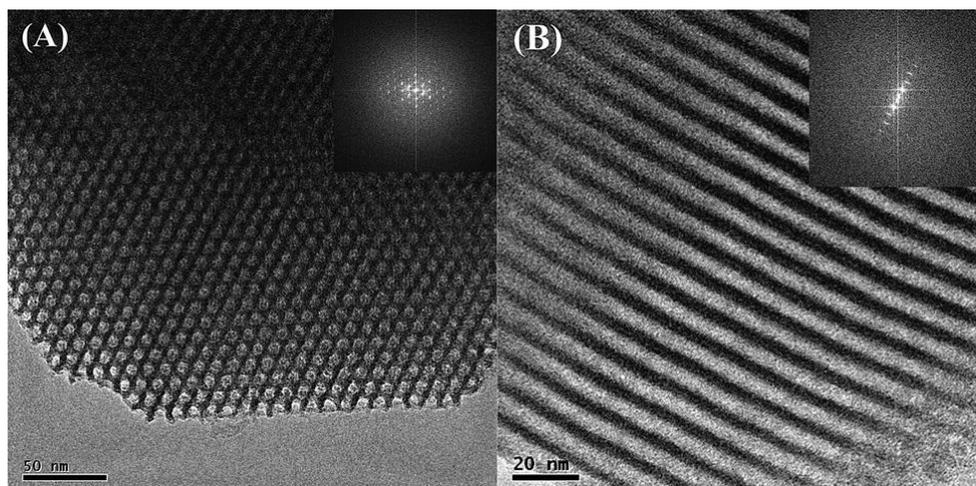


Figure 3. TEM images and the corresponding Fourier-transformed images for SBA-15 with the electron beam parallel (A) and perpendicular (B) to the nanochannels. Reproduced from Ref. [82] with permissions from the Royal Society of Chemistry.

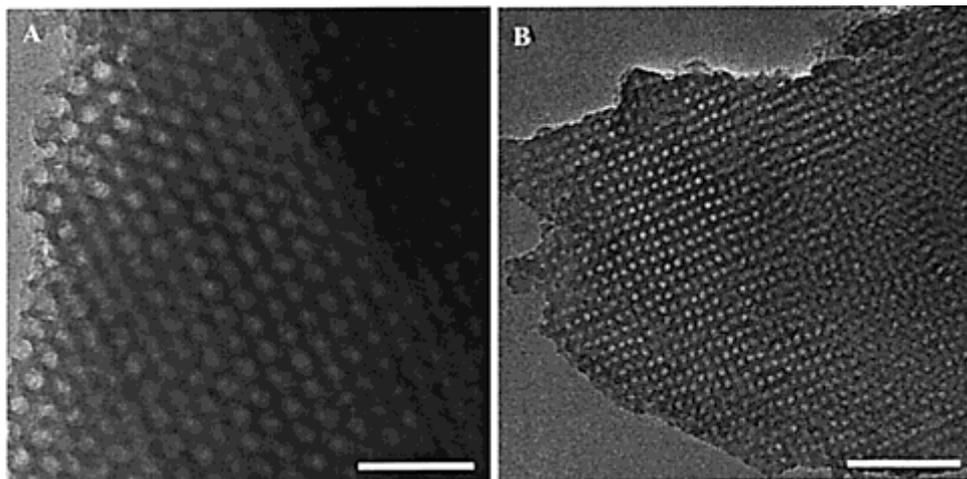


Figure 4. Representative TEM images of the calcined silica films templated by PS₂₁₅-*b*-PEO₁₀₀ (A) and PS₃₅-*b*-PEO₁₀₉ (B). The volume ratios of the silica/block-copolymer are both 60/40. Scale bars are 100 nm. Reproduced from Ref. [91] with permissions from the American Chemical Society.

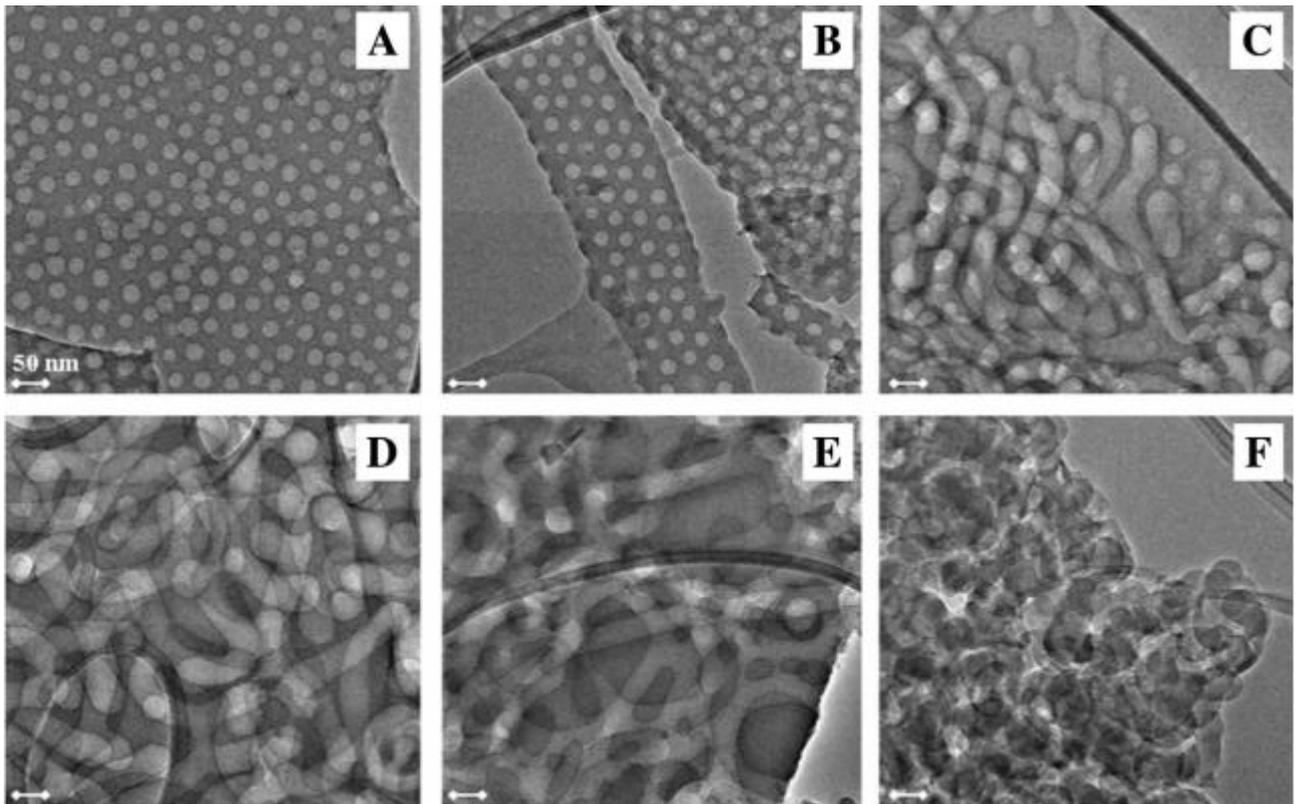


Figure 5. TEM micrographs of calcined films templated by using PS₅₆₇-*b*-PEO₇₀₄ and decreasing the TEOS/block copolymer weight ratios: 95/5 (A), 93/7 (B), 90/10 (C), 88/12 (D), 85/15 (E) and 75/25 (F). All the micrographs were collected at the same magnification. Reproduced from Ref. [94] with permissions from Elsevier.

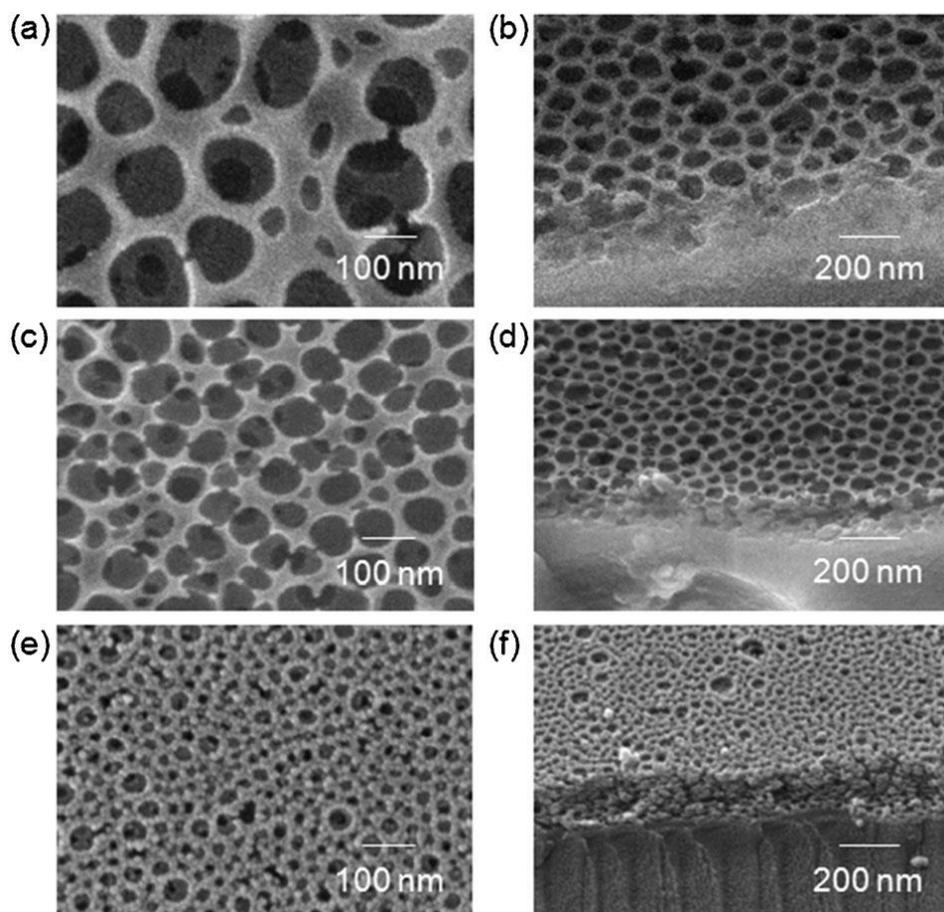


Figure 6. Top-view (left) and tilted 60° (right) SEM micrographs of PS₉₆₂-*b*-PEO₃₄₀₉ (A, B), PS₅₆₃-*b*-PEO₁₆₁₄ (C, D) and PS₃₈₅-*b*-PEO₁₂₀₅ (E, F) soft-templated titania films. Reproduced from Ref. [95] with permission from the PCCP Owner Societies.

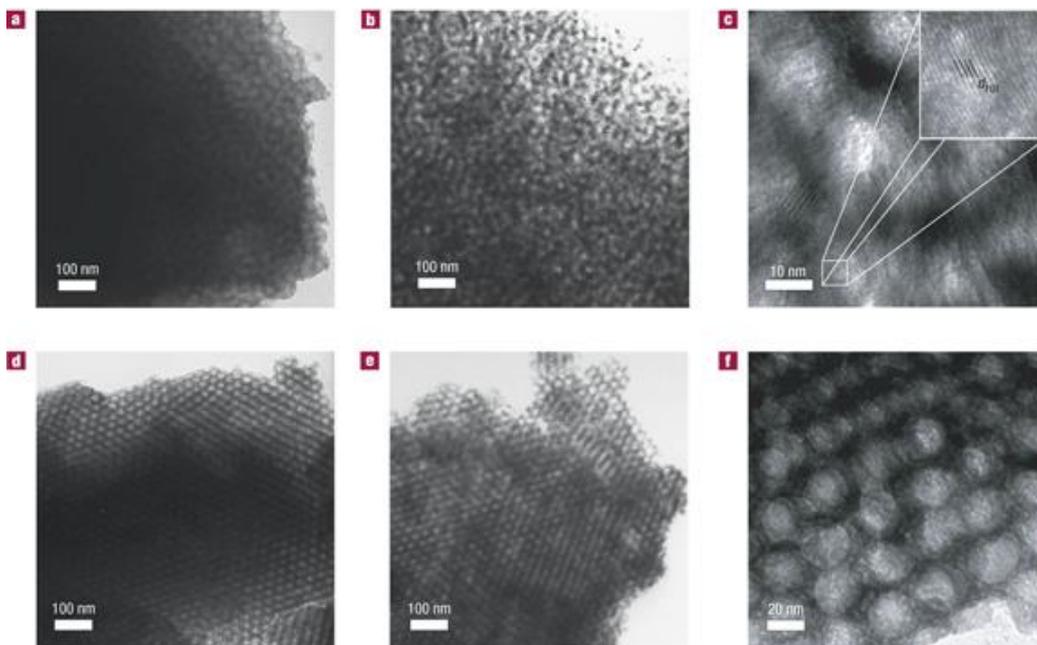


Figure 7. TEM micrographs of TiO_2 before (A) and after (B,C) heat treatment in air at low (B) and high magnification (C), respectively. Inset in (C) showing d_{101} spacing, $d_{101}=3.48 \text{ \AA}$, of the anatase structure consistent with literature values ($d_{101}=3.52 \text{ \AA}$ from JCDPS). TEM micrographs of Nb_2O_5 before (D) and after (E,F) heat treatment in argon at low magnification (E) and in air at high magnification (F), respectively. Reproduced from Ref. [97] with permissions from the Nature Publishing Group.

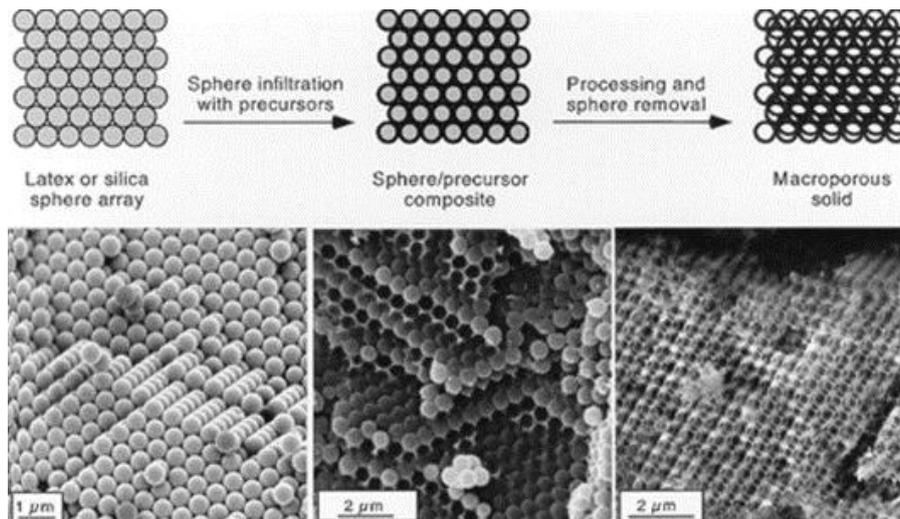


Figure 8. General synthesis scheme for periodic macroporous solids and the corresponding scanning electron micrographs (SEMs) for a PS/silica system prepared with TEOS. Reproduced from Ref. [45] with permissions from Elsevier.

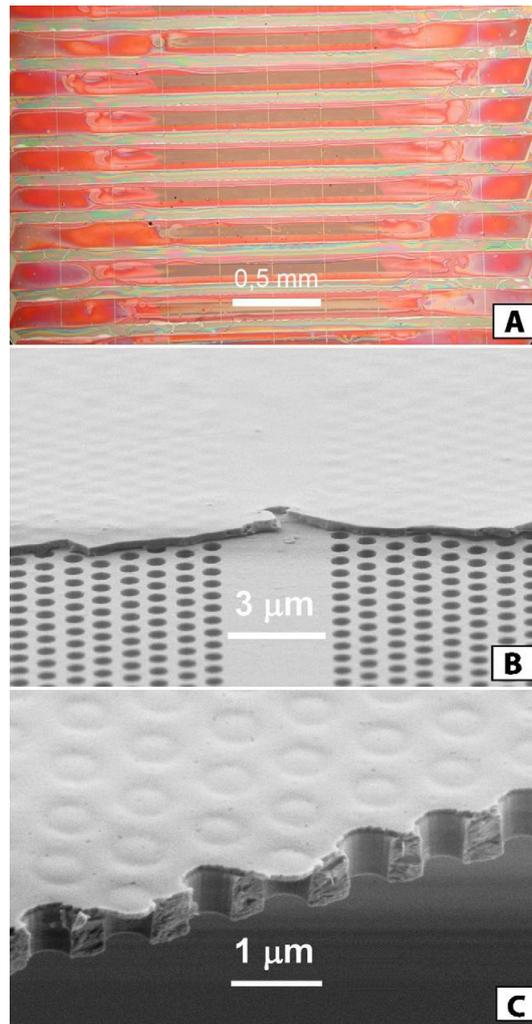
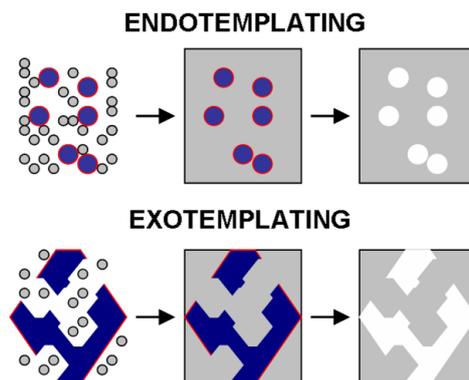
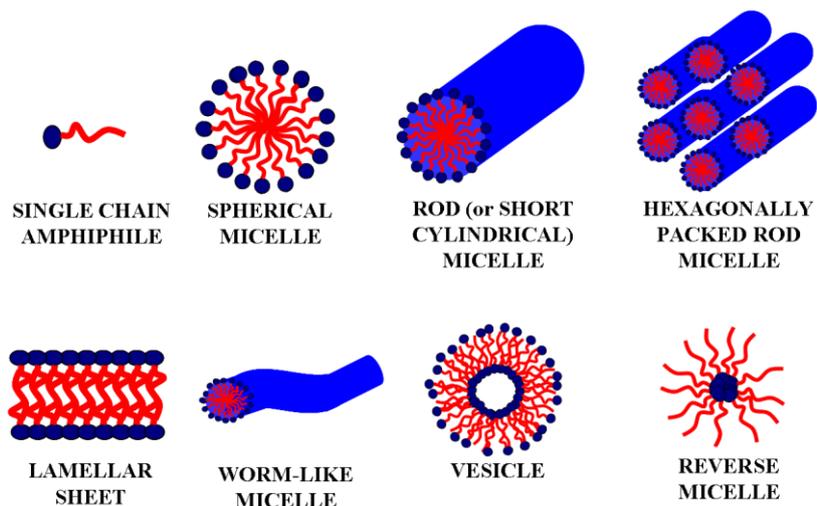


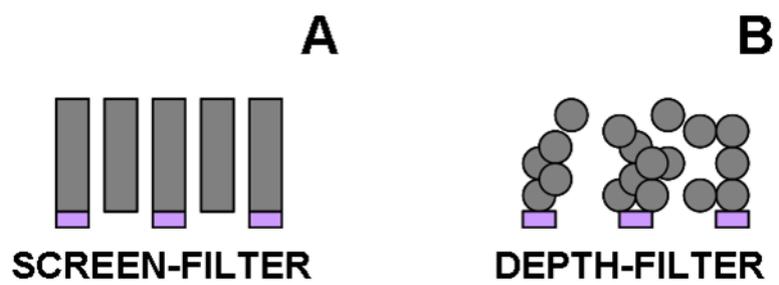
Figure 9. Images of the silica coated microsieve. (A) Optical microscope image of the macroporous substrate with the silica membrane after heat treatment. (B) SEM image of the macroporous substrate with a self-standing silica membrane after heat treatment. (C) SEM image of the self-standing silica membrane at high magnification. Reproduced from Ref. [22] with permissions from Elsevier.



Scheme 1. Comparison between endo- (soft-) and exo- (hard-) templating approaches for the synthesis of porous nanostructured materials. In endotemplating, the templating species are occluded in the forming solid, whereas in exotemplating, a rigid porous solid is infiltrated within the precursor network. In both routes, templating agents need to be removed, leaving a porous material.



Scheme 2. Schematic representation of different micellar architectures. Hydrophilic polar heads are indicated in blue, whereas hydrophobic non-polar tails are reported in red. Reproduced from Ref. [73].



Scheme 3. Schematic representation of a cross section of a screen-filter (A) and a depth-filter (B).