CHEMISTRY OF MATERIALS

REVIEW

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Hierarchical Mesoporous Films: From Self-Assembly to Porosity with Different Length Scales

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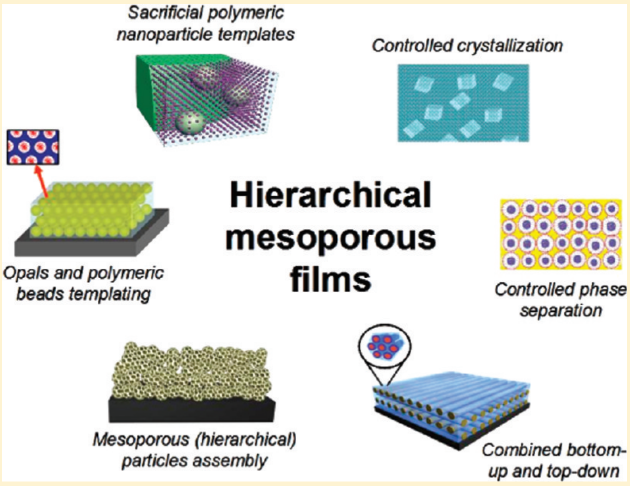
ABSTRACT: Hierarchical porous films are formed by interconnected pores of different dimensions, and are particularly attractive for the development of smart materials with multiple functions and enhanced transport properties. We have focused this review on hierarchical porous films whose synthesis, at least at one scale of porosity, is based on self-assembly. Several strategies have been proposed for the preparation of hierarchical porous films which for bulks and monoliths are more difficult to obtain. These materials represent a step further in the fabrication of complex materials through self-assembly, and achieving order through templating routes at different length scales is the ultimate goal.

KEYWORDS: mesoporous, films, hierarchical materials, self-assembly



INTRODUCTION

Hierarchical structures are widely diffused in nature;[1] wood for instance is a cellular material which scales from micrometers to centimeters while bones have different structures from few nanometers to centimeters[2] and diatoms exhibit hierarchical three-dimensional (3D) micro- or nanostructures.[3] Hierarchical materials in nature are formed through self-construction or self-assembly of building blocks into more complex structures.[4] Porous materials can also show a hierarchical porous structure, which means that in the same material pores of different dimensions should be present; in nature we have again the example of wood, diatoms, and sponges. The pores of a solid are classified by their pore size as micropores when they are smaller than 2 nm, mesopores when in the range of 2 and 50 nm, and macropores when above 50 nm;[5] a hierarchical porous material should exhibit at least a bimodal pore size distribution. The distribution of size, shape, and organization of the pores is directly related with the properties of the material and its capability of carrying out a specific function, such as sensing or catalysis. Furthermore, while the pores can be randomly distributed within the material, controlling of the order-disorder pore structure[6] allows opening a new set of properties and material performances, especially when pore order is controlled at the nanoscale.[7] The key issue for the synthesis of porous materials is how to template the pores, and if necessary how to order and shape them. Several strategies have been proposed to produce porous materials via templates,[8] which are removed after the material processing, or controlled phase separation.[9] A templating strategy is also at the base of the self-assembly through evaporation which allows preparing mesopores with an ordered and controlled organization via a combination of sol−gel and supramolecular chemistry.[10] This process can be combined with other strategies to obtain hierarchical porous materials which exhibit organization at least in one length scale.[11] Nakanishi et al.,[12,13] and Huesing et al.[14] have synthesized hybrid organic-inorganic monoliths with continuous macropores formed by phase separation along with micro- and mesopores which are templated by micelles formed by an amphiphilic triblock copolymer. More recently, the formation of an organic polymer simultaneously to self-assembly has been also developed as a synthesis route toward macroporous-mesoporous monoliths.[15] The fabrication of hierarchical porous materials has been also extended to obtain films with different pore length scales.[16] Controlling of the pore properties is, however, more difficult to achieve in films because the fast evaporation of the solvent makes the process kinetically controlled, and the chemistry has to be carefully modulated to get self-organization.[17−19] If hierarchical

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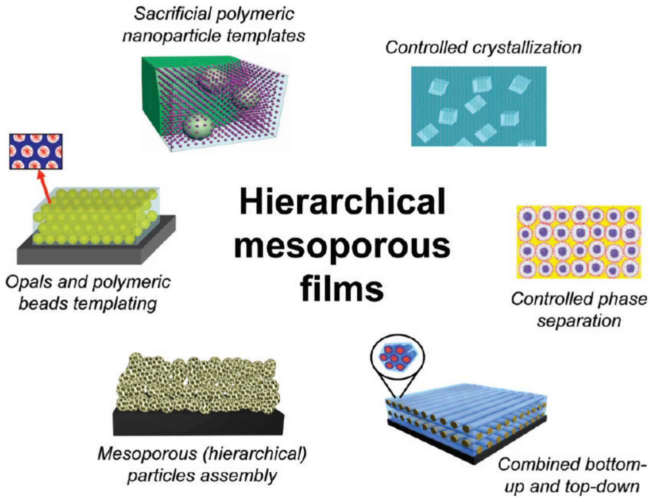

Figure 1. Illustration of the main synthesis and fabrication routes that have been used to obtain hierarchical porous films by combining self-assembly with other templating strategies.

porous films are synthesized by self-assembly to obtain organized mesoporosity, the other templates should not interfere with self-organization.

We have focused this review on hierarchical films which exhibit mesopores which are produced through self-assembly. Even if different other strategies have been successfully applied to obtain hierarchical porous films, which use for instance multiple templating, the self-assembly route beside its elegance opens the true possibility of fine controlling of the porosity and building complex controlled porous materials. A general illustration of the main synthesis and fabrication routes that have been used to obtain hierarchical porous films by combining self-assembly with other templating strategies is reported in Figure 1. The review has been divided in different paragraphs for each different synthesis route, with one specific section for titania films.

HIERARCHICAL SILICA FILMS FROM MESOPOROUS SILICA NANOPARTICLES

a. Mesoporous Hierarchical Particles. An interesting strategy for making hierarchical mesoporous films is the use of nano or microparticles with hierarchical porosity[20] for obtaining coating layers. This route has some advantages because it allows controlling two important properties of the film, the porosity and the surface roughness. Tuning of the film roughness is, in fact, possible by changing the particle shape and dimension; this gives the important advantage that some surface properties such as hydrophobicity and hydrophilicity of the coating can be easily designed.[21] This route has been exploited for producing self-cleaning antireflective coatings[22] and layers with superhydrophobicity and superhydrophilicity properties.[21] Silica coatings with hierarchical porosity have been fabricated using silica nanoparticles with hierarchical porosity[23] as building units; silica nanoparticles with a size of 150−220 nm with a bimodal distribution of porosity and pores of 5−30 nm and smaller mesopores of 2−3 nm in diameter after calcination have been employed. The pores of smaller dimensions have shown, in general, an ordered topological structure while the pores of larger dimensions remain disordered. The porosity has been produced using an ionic surfactant, cetyltrimethylammonium bromide (CTAB), and controlling the volume ratio of the cosolvents. A layer-by-layer deposition has been used to fabricate silica films[24] that after modification of the surface by 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane have shown superhydrophobic properties.[21]

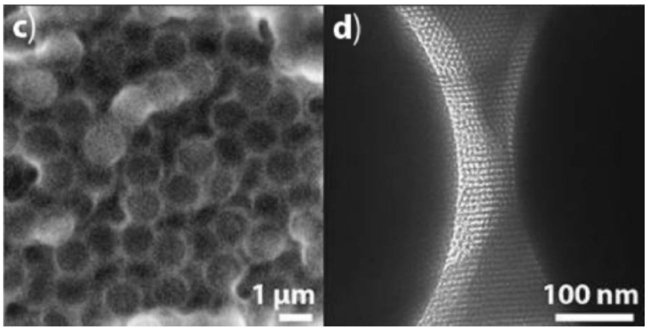

Figure 2. Scanning electron microscopy (SEM, c) and transmission electron microscopy (TEM, d) images showing the composite structure of spheres within the silica matrix. The TEM image shows the mesoporous structure in the silica matrix which is used to embed the particles. The images are taken from Figure 7 in ref 21 with permission. Copyright 2010 American Chemical Society.

b. Mesoporous Particles Assembly. Silica mesoporous particles can be also used as the building units for preparing hierarchical mesoporous films. A quite sophisticated strategy has been developed by Li and Stein for the fabrication of a hierarchical porous silica film by incorporation of functionalized porous silica spheres into the matrix.[25] At first monodispersed mesoporous silica spheres have been prepared and functionalized with organic probe molecules for visual Cd^{2+} ion detection; in a second step core-shell particles have been obtained by coating the mesoporous spheres with a thin layer of polymethylmethacrylate (PMMA). Finally the core-shell particles have been redispersed in a silica sol with Pluronic F127, to deposit a film and obtain a hierarchical porous structure (Figure 2). The role of PMMA is to protect the functionalized mesoporous spheres from the penetration of silica sol during the assembly step, which could eventually results in pore blocking and or reaction with the surface functional species. The removal of the polymer and surfactant from the film does not affect the organic probe molecules within the silica spheres, and functionalized hierarchical porous silica films are finally obtained. A color change of the film after exposure to analyte solutions with low concentrations of Cd^{2+} ions has confirmed that the confined probe molecules remained active after the multiple processing steps and that they are accessible via the mesopores that surround the embedded silica porous spheres.

ONE-POT TEMPLATING USING NANO AND COLLOIDAL POLYMERIC PARTICLES

a. Hierarchical Porous Silica Films from Sacrificial Polymeric Nanoparticle Templates. Pores of well-defined dimension and shape can be templated by using sacrificial particles;[26,27] the particles are generally introduced in the precursor solution and removed after film processing by thermal treatment. This route has the clear advantage that the geometrical properties of the templating structure can be well designed in advance and that at the same time the surface of the templating particles can be changed according to the synthesis need. On the other hand if the templating particles are in the nanoscale a series of difficulties have to be faced because nanoparticles tend to aggregate and homogeneous dispersion, without phase separation and clustering, has to be achieved. The fabrication of films through liquid phase deposition gives in any case the advantage of a quite flexible route, and control of the solvent, pH, and concentration is used to disperse the particles in the solution. In general, the particles are at first synthesized and dispersed in a proper solvent to obtain a colloidal solution which is then added to the precursor sol which contains the other template, a block copolymer or an ionic surfactant. Much care has to be taken to obtain a homogeneous dispersion of nanoparticles and to choose a solvent which is compatible with the evaporation conditions during film processing. The organic polymer nanoparticles, after film deposition, can be finally removed via calcination at temperatures between 200 and 300 °C. The dimension and shape of the templated pores are slightly modified upon calcination because the thermally induced uniaxial shrinkage of the film slightly produces a shape deformation which becomes more elliptical (Figure 3). An example of this technique is the synthesis of hierarchical silica films with pores of different dimensions which are templated by a block copolymer (Pluronic F127) and polystyrene nanoparticles.[28] At the end of the evaporation-induced self-assembly (EISA) process a bimodal pore distribution is observed with organized mesopores with a body-centered tetragonal (*I*4/*mmm* in the space group) mesostructure, while the nanoparticles give pores of 70 nm. The nanoparticles result well dispersed, and the silica films exhibit an ultralow refractive index, 1.14, which is lower than the value measured for the monomodal mesoporous film (1.17). It is interesting to observe that the presence of the nanoparticles does not disrupt the EISA process and that order of the mesopores is maintained.

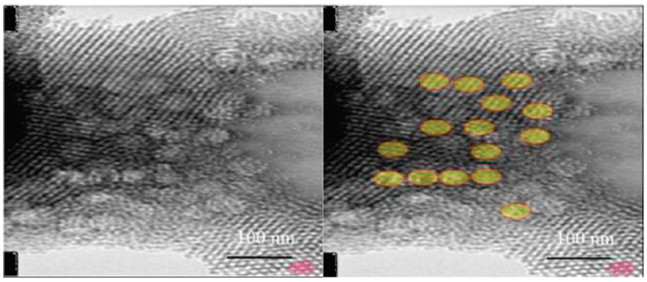

Figure 3. TEM image of mesoporous silica films after calcination at 350 °C; on the left side the elliptical pores which are formed upon calcination and removal of the templating polymeric nanoparticles are highlighted in yellow.

b. Hierarchical Porous Silica Films with Multimodal Pore. The fabrication of hierarchical porous films is not limited by the number of pore length scales that can be introduced in the material, and in principle multimodal porosity should be possible without limitation (Table 1). An example of multimodal porous materials has been shown by Smarsly et al. which realized a trimodal pore hierarchical bulk material with bimodal mesoporosity and a macroporosity.[29] The macropores have been templated by polysterene beads (100−400 nm) while the inorganic wall texture contained two distinguishable types of mesopores templated by block copolymers and an ionic liquid.[30,31] The larger spherical mesopores of around 12 nm in diameter have been attributed to the block copolymer (poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide), "KLE"), and the smaller mesopores in the 2−3 nm range to the ionic liquid (1-hexadecyl-3-methylimidazolium-chloride, $C_{16mim}Cl$). This approach has been successfully extended from bulk to films, and silica layers with different combinations of small and large mesopores and macropores have been obtained.[32] In this case the large macroporosity has been generated using polymethylmethacrylate (PMMA) colloidal particles. The hierarchical silica films have been prepared through one-pot synthesis and EISA processing via dip-coating; bimodal (KLE-IL and KLE-PMMA) and trimodal porous (KLE-IL-PMMA) materials have been finally obtained. The trimodal porosity is characterized by worm-like mesopores of around 3 nm templated by the ionic liquid, spherical mesopores of around 14 nm formed by KLE surfactant, and macropores of 120 nm of diameter generated by the PMMA

Table 1. List of the Hierarchical Porous Films with the Pore Length Scale and the Templating Agents

material	hierarchical porosity	mesopore template	porogen material	ref.
silica films with bimodal h.p.	5 nm, 15−20 nm	Pluronic P123 CTAC	cellulose nitrate	30
silica films macro-mesop.	3−11 nm, 350 nm	polyoxoethylene lauryl (or cetyl) ether PS-b-PEO (SE30/30)	cellulose acetate and polyamide membranes	32
silica films with controlled surface properties	2−3 nm, 5−30 nm	CTAB	cosolvents	16
silica films bimodal	5 nm, 70 nm	Pluronic F127	PS nanoparticles	24
trimodal silica	3 nm, 14 nm, 120 nm	Pluronic F127 KLE	PMMA nanobeads	28
bimodal meso-macro	3 nm, 100 nm	CTAB	polystyrene nanobeads	34
trimodal hierarchical silica, titania, niobia	10 nm, 100 nm, 1000 nm	Pluronic F127 Pluronic P123	polysterene spheres micromolding	39
bimodal silica	450 nm, 2 nm	CTAB	polystyrene spheres	36
silica hierarchical shape controlled	2 nm, 270 nm (cubes)	Pluronic F127	mixed salts: Na_2HPO_4, NaCl	40
trimodal hierarchical silica, shape controlled	6 nm, 100−280 nm (cubes), 100 nm	Pluronic F127	Na_2HPO_4, NaCl, water	41
bimodal titania	52 nm, 180 nm	PDMS-b-MA(PEO)	PMMA	48
bimodal titania	5 nm, 80 nm	Pluronic F127	polysterene nanobeads	49
bimodal titania	2 nm, 0.1−2 μm	Pluronic F127	poly(ethylene glycol)	52
bimodal titania	13−18 nm, 20−150 nm	Pluronic F127	poly (propylene glycol)-THF	53

colloidal particles. At the end of the process the KLE templated mesostructure maintains a high level of organization even in presence of IL and PMMA. The electrochemical performances of the films have been also tested by grafting active ferrocene groups onto the pore walls; a high electrochemical response due to the interpore connectivity and high surface area has been observed.

HIERARCHICAL POROSITY USING CELLULOSE NITRATE AS POROGEN MATERIAL

An alternative material as pore generator is cellulose nitrate that has been used to produce hierarchically porous silica films with bimodal distribution.[33] Cellulose nitrate is a high energetic material which undergoes deflagration under strongly reducing conditions; the gas stream which is produced during decomposition of cellulose generates a porosity within the material. The lower temperatures of deflagration of cellulose nitrate with respect to combustion synthesis allows forming the pores when the silica films still have a low viscosity. The method has allowed the synthesis of silica films of around 500 nm in thickness with a surface area of 510 m^2 g^{-1} and a bimodal pore size distribution with large pores of 15−20 nm and small pores of around 5 nm. The 5 nm pores are templated by surfactant micelles while the larger 15−20 nm pores are the result of the outgassing from the cellulose nitrate decomposition. Both ionic and nonionic surfactants have been employed, and the low angle X-ray diffraction patterns have shown that the mesoporosity has a well-defined structure.[34] It is interesting to observe that the presence of the surfactant is necessary not only to generate the pores of smaller dimensions but also to obtain an efficient dispersion of cellulose nitrate; attempts to make mesoporous films without the surfactant have, in fact, failed. A side effect of this synthesis is the formation of a harder skin on the surface with a self-sealing surface phase.[35]

POLYMERIC MEMBRANES AS TEMPLATES FOR MACROPOROUS-MESOPOROUS STRUCTURES

A bimodal distribution in the meso and macroscale (pores in the micrometer range) in silica films can be achieved using cellulose acetate or polyamide membranes for the templating of the macropores.[36] In this case a polymeric membrane, which has a porous structure in the micrometer range, is impregnated with a mesoporous templating solution; the membrane is then deposited on a substrate, dried, and after calcination a silica film of several micrometers in thickness and hierarchical porosity is finally obtained. The mesopore dimensions have been controlled by the choice of the porogen, nonionic surfactants, such as polyoxyethylene(10)lauryl ether or polystyrene(PS)-b-Polyethylene(PE) oxide. The final hierarchical material has shown mesopores (3−12 nm) and macropores of 350 nm of diameter with a surface area from 473 to 856 m^2 g^{-1}. The mesopores are not ordered but the material exhibits two orders of porosities which result well interconnected.

OPALS AND POLYMERIC BEADS TEMPLATING

Polymeric particles offer several opportunities for templating pores from meso to macro scale into silica films; several strategies have been used (vide supra) which are in general based on one pot processing. The particles are added into the precursor sol and dispersed in the matrix; after removal they leave pores from nano to macro scale as a function of the templating particle dimension. Combining self-assembly of surfactants or ionic liquids with polystyrene templating, silica-based materials with both interconnected macroporous and mesoporous structures have been obtained.[37] Following this specific approach the main issues that have to be faced are a good dispersion of the particles, avoiding aggregation which in case of nanoparticles is a main problem, and controlling the dimension without significant size dispersion. Polymeric beads allow also the formation of layers of particles, such as in the case of microparticles which give the beautiful organization into opal structures. Not only ordered layers of polymeric beads can be formed but simply two-dimensional (2D) layers without any organization into 3D structures, such as a monolayer of particles without any in-plane organization. The voids between the particles can be filled with templating solution that allow to embed mesopores into the pore walls.

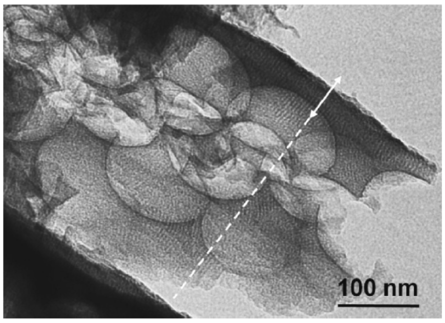

Figure 4. TEM image of the cross-section of a silica hierarchical porous film obtained using polysterene beads and electrochemical deposition. The arrow indicates the direction normal to the substrate. The image is taken from Figure 5 in ref 34 with permission. Copyright 2007 American Chemical Society.

a. Polystyrene Beads and Electrochemical Deposition of Mesoporous Layers. An example of such a type of strategy has been reported by Etienne at al.[38] which have obtained thin films with combined macropores and mesopores by the electro-chemical deposition of mesoporous silica within the voids of an assembly of polystyrene nanobeads. Electro-assisted chemical deposition in combination with a surfactant templating process can be successfully applied to produce mesostructured films with a well-defined organization of the porosity; in particular the method allows obtaining vertically aligned (with respect to the substrate) mesochannels in the silica films.[39] A polystyrene beads assembly has been deposited on an ITO substrate, and the interparticle voids have been filled with mesoporous silica layers using an electrochemical route. Modulating the deposition conditions has allowed tuning of the silica layer on the particles; the interesting feature is that in accordance with what is observed in the case of silica mesoporous films produced by electrochemical routes, a texture of the silica mesostructure is observed also in this case (Figure 4).

b. Opals and Hierarchical Porous Films. The use of colloidal crystals as a template for the preparation of hierarchical porous films has the advantage that a 3D order at the macroscale is directly produced in the final materials. In general the strategy is based on a three step process, preparation of a colloidal crystal film using polymeric beads, infiltration of a mesoporous material precursor solution within the voids between the opal spheres, and finally removal of the surfactant and beads templates. The opal structure is produced via self-assembly of monodispersed colloidal particles, which is also a self-organization process driven by the evaporation of the solvent; the opal is, in fact, obtained via dip-coating in a solution of colloidal particles. An oxide film with

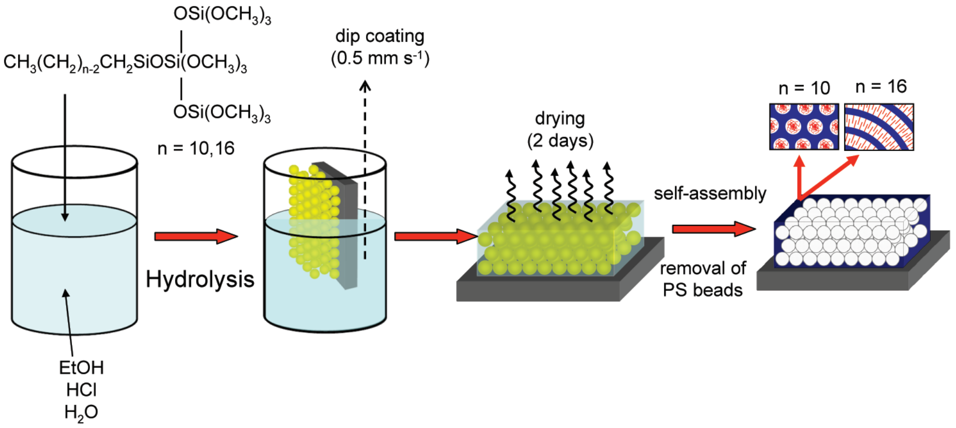

Figure 5. Illustration of the synthesis of mesostructured silica-based hybrids with ordered macropores. The image has been redrawn from Scheme 1 in ref 38 with permission. Copyright 2010 American Chemical Society.

ordered macroporosity and mesostructured porosity in the pore walls is the final product; in general, a bimodal meso-macro porosity is obtained via this route. Some examples of this approach have been reported in the literature and also some applications, such as TNT chemosensors have been proposed;[40] the optical response of monodispersed colloidal mesoporous silica opals has been also tested.[41] Kuroda has also infiltrated in the polystyrene particles voids, using spin-coating, a sol composed of oligomeric siloxane precursors bearing alkyls chains ($C_nH_{2n+1}Si(OSi(OCH_3)_3)_3$), and either a 2D-hex mesophase or a lamellar structure have been observed as a function of the alkyl chain length of the precursors[42] (Figure 5). After calcination the 2D-hex organic-inorganic hybrid generated a bimodal hierarchical ordered porous silica film with both macro- and microporosities.

c. Order at Different Length Scales. An example of multiscale self-assembly to obtain hierarchically ordered oxide films has been obtained by combining micromolding, polystyrene sphere templating, and EISA with block copolymers as surfactant.[43] The final materials have shown hierarchical ordered porosity with discrete length scales of 10, 100, and 1000 nm in a single matrix. Structural organization over the three independent length scales has been realized by combining block copolymer micelle templating through EISA (10 nm), latex sphere templating (100 nm), and micromolding (1000 nm) to produce ordered mesopores (10 nm), macropores (100 nm), and surface micropatterns (1000 nm) (Figure 6). The mesopores show a cubic (using Pluronic F127) or hexagonal (with Pluronic P123) ordered structure while the polymeric spheres organize into a close packed array within the confinement of the micromold channel network. The interesting phenomenon of organization of the latex spheres in confined geometries is attributed to nucleation, which is driven by the capillary attractive forces between the microspheres and growth, because of evaporation and influx of suspension to compensate for the loss of solvent. This mechanism allows the combined formation of ordered macroporous structures (100 nm) together with ordered cubic arrays of mesopores (11 nm) in the silica framework.

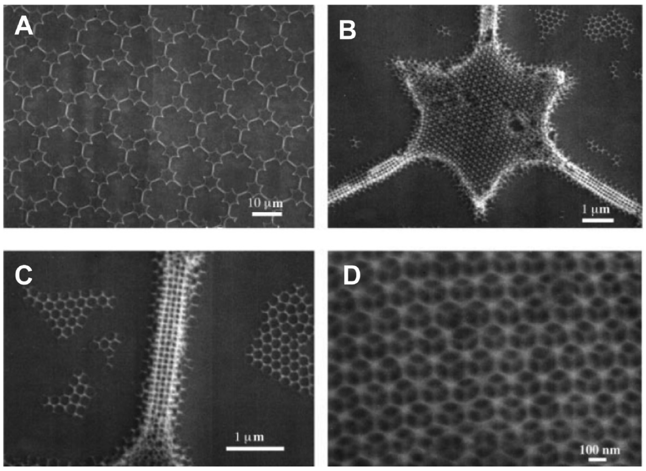

Figure 6. SEM images, at different magnifications, of hierarchically ordered mesoporous silica displaying organization over three discrete characteristic dimensions. The image is taken from Figure 3 in ref 39 with permission. Copyright 2009 Science.

■ SALT CRYSTALS AS TEMPLATE: CONTROLLING THE SHAPE OF THE PORES

The examples that we have previously reported show that hierarchical porous films are generally formed using templates with a spherical geometrical shape; even if after thermal treatment the pores can assume an elliptical shape questions arise about the possibility of templating pores of different shape in hierarchical materials. This possibility has been exploited by Malfatti et al. that have templated pores of cubic shape and nanodimension, so-called nanoboxes, through a controlled salt precipitation.[44] The films show a cubic ordered array of mesopores (body centered cubic, *Im*3*m* in the space group), templated during EISA by micelles of Pluronic F127, together with the presence of well-defined nanoboxes that appear homogeneously dispersed in the material. The formation of NaCl nanocrystals is driven by the evaporation of the solvent during film deposition while uncontrolled precipitation of the salt is avoided by the coaddition of Na_2HPO_4 in the precursor sol. A hierarchical porous silica film is obtained after removal of the salt by washing with water and surfactant by calcination; mesopores of spherical shape organized in a cubic array together with pores of cubic shape (100−280 nm) which are instead randomly distributed within the matrix are finally produced (Figure 7). This process also has the advantage that the pores can be selectively emptied in two separated steps by thermal treatment and water.

Using a similar approach the same group has also shown that combining the salt-template route with controlled phase separation, it is possible to obtain pores of spherical shape of larger dimensions

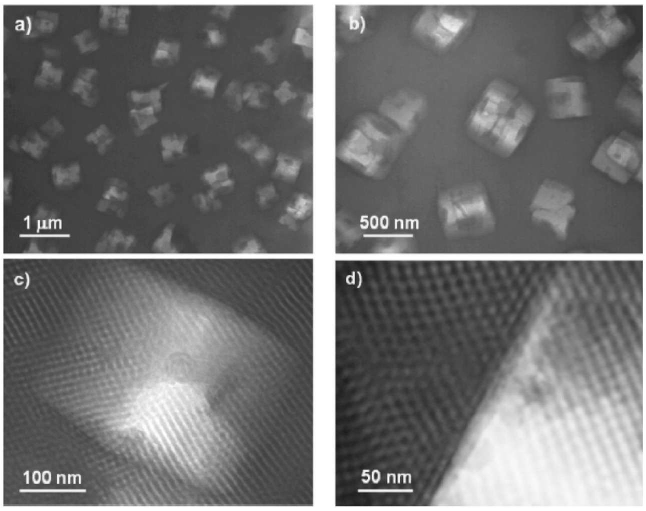

Figure 7. TEM images (a−d) at different magnifications of a film showing the presence of mesopores and nanoboxes. The image is taken from Figure 2 in ref 40 with permission. Copyright 2008 American Chemical Society.

together with the mesopores in the same film.[45] The dimensions of the nanocubes and nanospheres are in the 20−200 nm range and can be modulated through the film processing conditions. Only a very specific combination of different synthesis parameters, such as surfactant concentration and aging of the precursor solution, allows the formation of the pore templates. The phenomenon is controlled by the surfactant concentration and aging time of the precursor solution; at the end of the process pores of cubic and spherical shapes of two well-defined dimensions (mesopores and macropores) can be obtained in hybrid films.

PREPATTERNED SUBSTRATES AS MACROSCALE TEMPLATES

Texture in the macroscale can also be imparted by depositing mesoporous films onto substrates that are prepatterned with sacrificial meso- or microscale patterns. The use of orthogonal methods of template elimination permits to obtain thin films with macro-and mesoporous features. In a first example, mesoporous silica films have been deposited onto a macroporous titania thin film; the silica layer copied the macropore pattern while maintaining a high degree of pore ordering and accessibility. Exposure of this bilayer to acidic conditions results in the selective removal of the TiO_2 film, leading to a mesoporous structure that floats on macrocavities.[46] In the same vein, substrates can be prepatterned with tailored block copolymers that present vertically ordered domains. Deposition of a titanosilica-surfactant precursor solution by selective swelling of hydrophilic domains leads to mesoporous titanosilicate pillars that can be then covered with a dense layer.[47] These complex films present a double scale texture which has potential applications in microfluidics or lab-on-chip devices.

Dewetting processes can also lead to the straightforward production of micrometric or submicrometric substrate patterning. Zelcer et al.[48] developed a simple patterning method to produce carbonaceous droplet patterns by depositing a sucrose-surfactant solution in the presence of sulphuric acid. Upon drying, dehydration of the saccharide takes place, leading to the formation of a homogeneous pattern of submicrometer disk-like carbonaceous droplets with small size dispersion throughout all the substrate. A mesoporous silica film can be deposited on the top of the carbonaceous islands, leading to bump-like patterned mesoporous films. These films present two different mesopore orientations; film regions deposited on the substrate display an *Im*3*m* mesophase, with the [110] pore plane oriented parallel to the surface, as usually reported. On the contrary, the film regions deposited onto the islands present a different pore orientation because of constraints imposed by the surface topology. Carbon removal by thermal treatment leads to hierarchical films displaying mesoporous submicrometer sized cavities, or "nanovaults".[48]

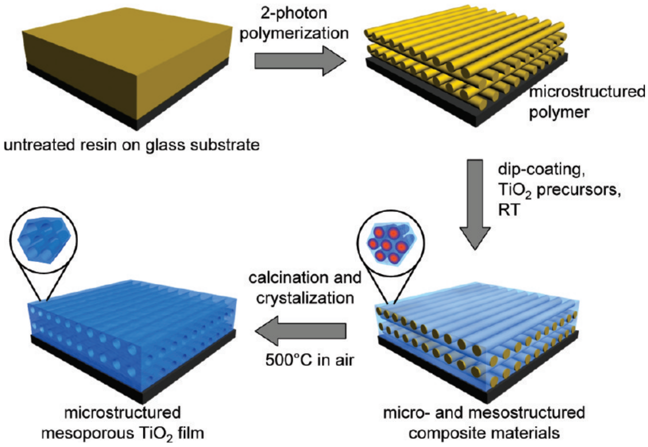

Figure 8. Illustration of the synthetic strategy for the combination of 2-photon polymerization and the self-organization process of mesostructured titania. The image has been redrawn from Figure 1 in ref 45 with permission. Copyright 2010 Springer.

HIERARCHICAL MATERIALS BY COMBINING BOTTOM UP AND TOP DOWN ROUTES

The integration of bottom up and top down routes for preparing nanoscale functional materials offers several advantages, and, even though it is not yet so fully exploited, represents an important trend in nanotechnology.[49,50] Laser microfabrication of complex polymeric structures can be integrated with a bottom up chemical route such as EISA for obtaining hierarchical porous films of well-defined geometry. 3D polymeric structures, such as 3D woodpiles, can be fabricated by two photons polymerization (2PP) with femtosecond laser technology[51] and used as a replica for mesoporous silica layers. After the deposition of mesostructured coatings on the polymeric framework, the organic replica is removed by calcination leaving a mesoporous structure which forms the frame of an ordered microporous scaffold (Figure 8). Because the 2PP allows fabricating a large variety of microporous 3D structures, integrating this technique with EISA gives the possibility of design hierarchical porous films with well-defined 3D geometries.

The same process has been also applied in a similar way to produce titania hierarchical films, and 3D hierarchical pore structures by a combination of laser-based templates and the self-organization process of mesostructured titania have been produced.[52] The macrotemplating polymer and the mesotemplating surfactant molecules are removed via calcination to obtain a replica of the initial polymer structure with a hierarchical (macro- and meso-) pore system. The calcination step produces also the crystallization of titania from amorphous to anatase.

TITANIA HIERARCHICAL POROUS FILMS

Most of the work on hierarchical porous thin films has been based on silica, which is the most used composition and whose chemistry is well-known. In the case of mesoporous thin films, however, silica has shown a small hydrolytical stability and chemical durability which represent a serious treat for several applications. On the other hand titania mesoporous films are much more durable and stable in aqueous environments,[53] but the chemistry is much more complex.

Titania Hierarchical Films for DSSCs. The possibility of fabricating hierarchical porous titania films is particularly challenging because several important applications such as dye sensitized solar cells (DSSCs) show an enhancement of the performances with the improvement of the transport properties within the material.[54] An example of fabrication of hierarchical titania porous films for DSSCs via self-assembly combined with sacrificial polymeric nanoparticles templating has been reported by Kaune et al.[55] They have used an amphiphilic diblock copolymer, poly(dimethyl siloxane)-block-methyl methacrylate poly(ethylene oxide) [PDMS-b-MA(PEO)], as structure directing agent, and PMMA colloidal particles as microstructure template.[56] The hierarchical porous structure films show a mesoporous disordered network with pores of mean size of 52 nm and macropores with a mean size of 180 nm. An efficient infiltration of the conductive polymer poly(N-vinylcarbazole) (PVK) in the porous network by solution casting has been observed.

Titania Hierarchical Films for Photocatalysis. Another important property of anatase titania films is their photocatalytic activity, which is used for different applications from self-cleaning coatings to water purification. Also in this case it is expected that hierarchical porosity in the meso-macro range could potentially improve the performances of the device. Kimura et al. have prepared titania hierarchical porous films using Pluronic F127 as surfactant template and polystyrene nanobeads of 100 nm of diameters as sacrificial template.[57] Interestingly the same group has also reported about the preparation of hierarchical titania films using an emulsion induced process to generate macropores (vide infra).[58] They have, however, preferred the polymer particle templating route for the photocalytic application because of the better control in terms of size and amount of macropores. After film deposition the mesopores show a cubic ordered array which is lost after calcination at 400 °C to remove the surfactant and the sacrificial nanoparticles. The nanoparticles that template the macropores show the tendency to aggregate and some clustering of macropores appear in the film. The photodegradation of methylene blue is effectively accelerated in hierarchical films because of effective diffusion of MB in the PS-derived macropores.

Titania Hierarchical Films via Phase Separation. Controlled phase separation is a very successful synthesis route which has allowed to fabricate hierarchically porous materials which have been optimized for high-performance liquid chromatography separations.[9] The process can be applied to different composition of oxides and hybrid organic–inorganic materials. Synthesis of hierarchical materials via phase separation can be extended also to thin films, in this case with the advantage of developing a one-pot route but the potential difficulty in controlling the phase separation. The fast evaporation of the solvent, in fact, makes difficult a precise control of the kinetics of the process, and the macropores tend to show a large dispersion in size.[45] A titania film with a cubic ordered mesophase and macropores has been obtained using a precursor sol of Pluronic F127 in water without ethanol with the addition of the hydrophobic 1,3,5-triisopropylbenzene. The emulsion which is formed induces the formation of macropores in the titania mesoporous film which can be crystallized into anatase without disruption of the ordered mesophase. It is interesting to notice that the emulsion induced templating seems not to interfere with the self-assembly of mesopores via micelle templating during EISA.

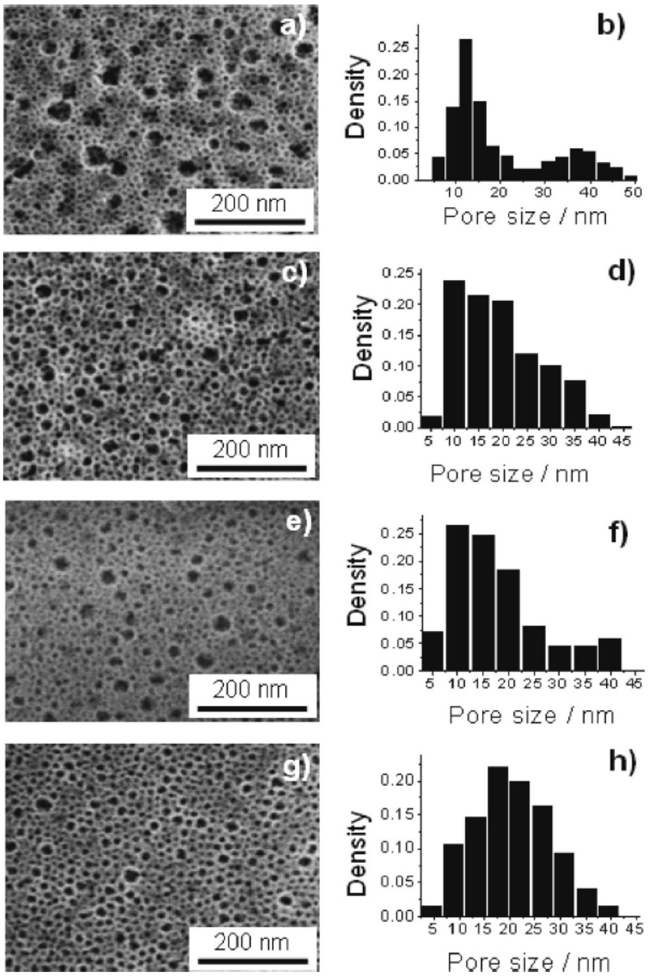

Figure 9. FE-SEM micrographs and relative pore size distributions of samples prepared as a function of the volume of THF (V_{THF}) maintaining constant the other synthesis parameters, ($P = [\mathrm{PPG}]/[\mathrm{Ti}] = 6.25 \times 10^{-3}$ and $S = [\mathrm{F127}]/[\mathrm{Ti}] = 4 \times 10^{-3}$). (a) $V_{\mathrm{THF}} = 0\%$; (c) $V_{\mathrm{THF}} = 17\%$; (e) $V_{\mathrm{THF}} = 29\%$; (g) $V_{\mathrm{THF}} = 37\%$. The image is taken from Figure 2 in ref 53 with permission. Copyright 2008 American Chemical Society.

Titania thin films with hierarchical pore structure (macropores and nested mesopores) have been obtained in one pot using controlled phase separation. In this case Poly(ethylene glycol) ($M_{\mathrm{w}} = 2000$) induces a phase separation upon film formation, producing disordered macropores with controllable diameters between 0.1 and 2 μm.[59] The titania films exhibit disordered mesoporous walls (2 nm diameter) which crystallize to anatase titania after controlled thermal treatment.

Another example of hierarchical porous titania films produced via phase separation has been reported by Malfatti et al.;[60] in this case self-assembly with surfactant to form mesopores during EISA is also used, but the pores are not ordered. The process allows, however, obtaining a good control of the porosity is terms of pore size distribution and dimension. Tuning of pore size distribution (bimodal, with small mesopores 13−18 nm diameter, and large pores 20−150 nm diameter) is achieved by controlling the solubility of a pore enhancement agent, poly(propylene glycol) (PPG), in the presence of a cosolvent. The phase separation induced by the addition of PPG to alcohol/water solutions containing titania precursors produces smaller mesopores and large mesopores. The addition of a cosolvent of intermediate hydrophilicity, such as tetrahydrofuran (THF), favors the dissolution of PPG in the micelles; in turn, a more uniform population of intermediate size mesopores is obtained. A tailored templating system with multiple characteristic lengths is generated in situ by balancing the PPG and THF relative content (Figure 9). Controlling the phase separation and micelle template swelling behavior of a surfactant/polymer/solvent/cosolvent mixture allows to obtain a controlled hierarchical porous structure within the titania films. This system has been used as a host for enzymes, demonstrating dramatically the need to control macropore size to obtain bioactive coatings. A large-size enzyme such as DNA polymerase could only be adsorbed in titania films presenting a hierarchical pore system of 13 and 35 nm pores, an optimized combination of pore size compatible with the enzyme dimensions, and pore accessibility. The DNA polymerase molecules are selectively located in the large-size mesopores; the whole biofunctionalized film is able to efficiently amplify DNA by a polymerase chain reaction. The engineered pore sizes and tailored interconnectivity at the nanoscale are the key to biofunctionalization leading to an efficient enzyme performance.[61]

CONCLUSIONS AND FUTURE OUTLOOK

In this short review we have tried to give a general overview of the recent achievements in the synthesis of hierarchical porous thin films. Up to now the main issue remains the control of the porosity, which means controlling the pore size, the pore size distribution, the pore shape, the pore interconnectivity, and finally the pore organization. Achieving a fine control of all these properties is clearly a challenging goal, but the different strategies that have been proposed so far give an important clue about what the possibilities are for tailoring the material property for the application. It should be pointed out that, in fact, synthesis routes toward these materials are not yet fully optimized, and the field is in its infancy. However, the synergy between sol−gel methods, supramolecular templating, and new macroscale templating techniques bring out different ideas and routes that begin to build a palette of tools for tailoring the material for the requirements of a specific application.[62]

The future challenge is extending the possibility of producing ordered and interconnected multiscale porous networks homogeneously distributed along large substrate surfaces. This has been shown to be possible using opal films but should be extended to multimodal porous structures and beyond the limit of dimensions of colloidal particles. One-pot self-assembly through EISA of different nanoscale objects is a nice possible option, keeping in mind that order should be obtained at different length scales. Critical aspects regarding this route imply the control of the macrotemplate dispersion within the drying and assembling process to avoid inhomogeneities due to colloidal agglomeration. Concerning macropatterning processes based on phase separation, the main limitation is the high sensitivity toward synthesis and processing variables. More detailed studies should be performed to ensure robust methods that can be extended to industrial applications. In particular, the strategy of producing macropore templates in a one-pot process by polymerization upon drying[15] seems promising. Attention should be paid to the possibilities brought up by phase separation induced by commercial polymers or by inexpensive biopolymers.[63,64] Substrate prepatterning methods by polymer deposition, dewetting, or even by photolithography[65] also provide a means to produce large homogeneous areas on which mesoporous materials can be deposited, presenting multiscale textures. Combination of top-down and bottom-up methods is with no doubt a powerful concept that will also help to develop these complex materials for applications related to electronic and magnetic devices. In addition to these well-established strategies, it would be worth to explore in-depth new macroscale templating possibilities such as the use of breath figures[66] or Ice Segregation Induced Self-Assembly.[67]

The next step is moving to applications, some of which have already been envisaged, in particular those related to microfluidics or the interactions with heavy biomolecules such as DNA, antibodies, enzymes, macromolecular complexes (lipoproteins, protein sugar complexes), or even full cell membranes. Hierarchically porous films present an enormous potential in such diverse fields as lab-on-chip components, membranes, catalysis, drug delivery, macromolecule sensing, high-throughput arrays, cell culture, or tissue regeneration. However, full exploitation in such advanced devices has yet to be reached through the development of robust, highly reproducible, and low-cost synthesis methods.

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