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REVIEW

Nanoparticles in mesoporous films, a happy marriage for materials science

Plinio Innocenzi · Luca Malfatti

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Abstract Mesoporous ordered materials, whose porosity is within the 2–50-nm range, are an ideal host for functional nanoparticles. Mesoporous thin films, in particular, offer a large variety of options for the fabrication of advanced materials and devices based on the host-guest combination of matrix nanoparticles. Nanocomposite mesoporous films embedding metal, oxide, and semiconductor nanoparticles have been prepared using as matrix oxides, mixed oxides, and organic-inorganic hybrids. The organization of the pores is an important peculiar property of mesoporous ordered films and allows producing nanocomposites whose nanoparticles follow a very specific array within the material. The main synthesis methods to obtain mesostructured films containing nanoparticles, together with their applications, are briefly introduced in the present review.

Keywords Mesoporous materials · Self-assembly · Sol-gel · Thin films · Nanoparticles · Synthesis

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Nicola Pinna, Executive Editor, Mike Roco, Editor-in-Chief

P. Innocenzi (✉) · L. Malfatti
Laboratorio di Scienza dei Materiali e Nanotecnologie (LMNT), CR-INSTM, Dipartimento di Chimica e Farmacia, Università di Sassari, via Vienna 2, Sassari, Italy
e-mail: plinio@uniss.it

Introduction

Mesoporous films are characterized by a pore size in the range of 2–50 nm and a pore topology, which depends on the conditions of synthesis and processing (Soler-Illia et al. 2002; Brinker et al. 1999). Pores can be arranged in different ordered nanoarchitectures and assume 2D in plane or 3D configurations (Innocenzi et al. 2009). Mesoporous ordered films are produced by using a surfactant template and in general block copolymers (Deng et al. 2013) whose micelle formation and organization during the evaporation phase produce an ordered structure (Sánchez et al. 2008). In the film post-deposition processing stage, the template is removed and the framework structure is consolidated typically by a thermal treatment and the consequent removal of the template. This process is now well understood, and films with a large variety of porous mesostructures are currently fabricated.

The mesophases can be divided in two groups with a lower (2D phases) and a higher symmetry (3D phases). The failure in getting order generally is reflected in the rise of a worm-like phase, which forms when the condensation rate of the inorganic or hybrid precursors is too high to allow controlled self-assembly of the micelles. These disordered structures with a random distribution of the mesopores obtained via self-assembly have been also used for some applications even if the advantage of the pore organization is lost.

Mesoporous ordered 2D structures can be produced in the form of lamellar or 2D-hexagonal (2D-hex) phases, with the possibility of orienting the channels with respect to the substrates. The most common 2D porous phases are the hexagonal plane group *p6mm* and the planar rectangular *c2mm* mesophase. Even if in general the 2D phases are less stable than the corresponding 3D phases, they can be used to fabricate thin films whose pores are oriented with respect to the substrate.

Cubic structures have been reproduced with different types of cells: primitive cubic phase, $Pm\bar{3}n$ space group; bicontinuous cubic, $Pn\bar{3}m$; body centered cubic phase, $Im\bar{3}m$; body-centered tetragonal phase, I4/mmm; face-centered cubic phase, $Fm\bar{3}m$; and a double-gyroid cubic phase with space group $Ia\bar{3}d$ (Fig. 1).

The structural backbone can be in the form of oxide, mixed oxides, or even hybrid organic-inorganic. Another possibility is also to obtain crystalline pore walls; this has been reported in the case of hybrid mesoporous materials when employing bridged silsesquioxane precursors even if in films is more difficult to achieve (Carboni et al. 2015).

Mesoporous films have been tested for many applications in different fields by exploiting the properties of the large and ordered porosity or by producing functional materials for optical and electrochemical devices (Innocenzi and Malfatti 2013). In the last case, the porosity has been mainly used to host functional species, such as for instance optically active molecules or nanoparticles (Angelomè and Liz-Marzan 2014). The organized porosity represents an extraordinary host for nanoparticles, because it gives the possibility of forming ordered arrays on nanoparticles with controlled dimensions and even in some cases controlled shape. Another advantage is that the final material containing the nanoparticles can be designed in different ways with a large flexibility. Many strategies have been envisaged to introduce pre-formed particles or to form them in situ via one-pot synthesis or post-deposition processing of the material. The different combinations of synthesis, pore dimension and topology, and composition of the pore walls make mesoporous ordered films an ideal matrix for growing a large variety of nanoparticles, such as transition metal and metal oxide nanoparticles, quantum dots, and metallic particles with plasmonic properties. In the present review, we shortly introduce some of the most common methods of fabricating metallic, semiconductor, and oxide nanoparticles in mesoporous films and the main possible applications.

Synthesis of mesoporous films with nanoparticles

The production of mesoporous ordered films containing nanoparticles can be basically divided into two main lines, top-down syntheses, by employing external sources of radiation, or bottom-up syntheses, via chemical routes or impregnation of preformed materials. The choice among the different routes depends on the type of application to be developed. If patterning is required, for instance, the top down methods have the intrinsic advantage to allow an easy writing of the film (Innocenzi et al. 2007), while chemical syntheses do not require expensive equipment and reduce the number of fabrication steps. We will briefly revise some of the main synthesis routes in the following paragraphs.

Top-down methods

These methods are generally based on the exposure of the mesoporous film to an external source of light of different intensities and nature. The precursors required to obtain the nanoparticles can be both introduced in the sol during the film synthesis or impregnated into the pores after film deposition. Several sources have been used, such as UV radiation, hard X-rays, and laser lights, each one with specific characteristics. The selection of one of these sources depends on their availability, the costs, the properties which are required, and the eventual need to pattern the films.

Hard X-rays

Exposure of as-deposited oxide and hybrid organic-inorganic sol-gel films to an intense light source of several keV generated by a synchrotron storage ring produces densification of the films without any side effect, such as cracks or delamination (Innocenzi et al. 2011). The large number of free radicals produced upon exposure to hard X-rays induces the condensation of the oxide via hydroxyl removal and cleavage of the covalently bonded functional groups. At the same time, the free radicals can be used to produce in situ nanoparticles allowing a direct writing of the mesoporous films (Malfatti et al. 2010). The advantage of the method is the integration of the bottom-up and top-down routes, which is particularly suitable for soft matter

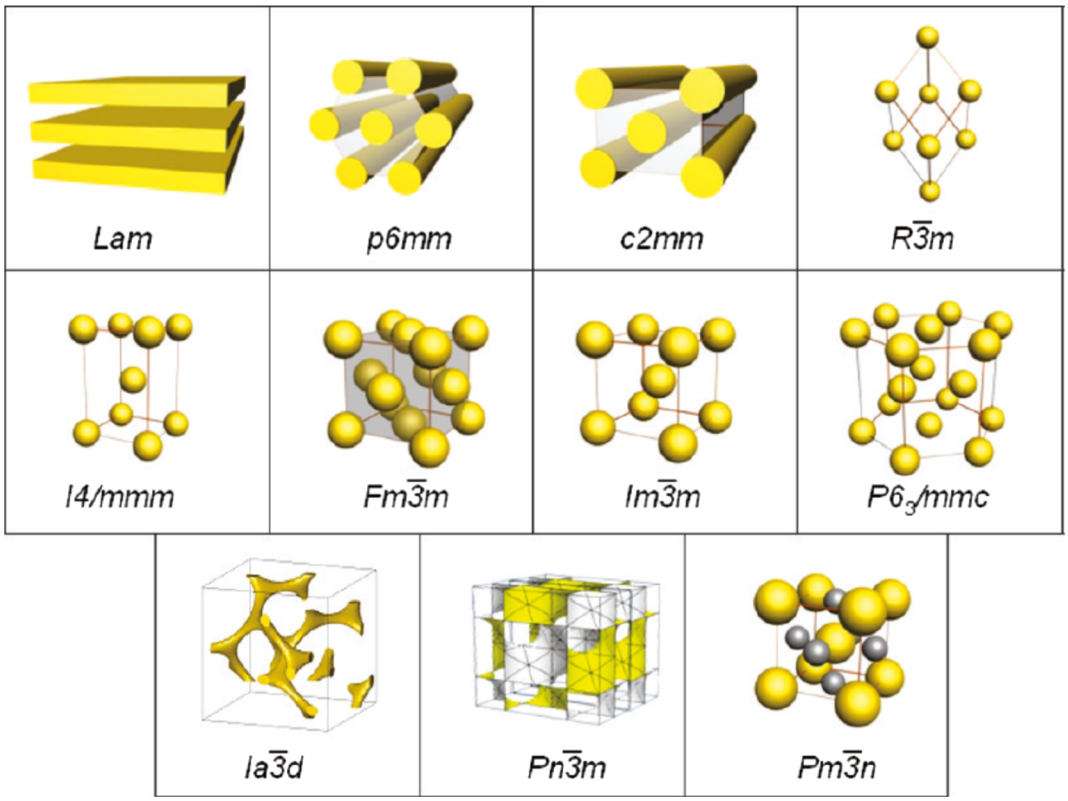

Fig. 1 2D (Lam = lamellar, p6mm, and c2mm), 3D (R3m, I4/mmm, Fm$\bar{3}$m, Im$\bar{3}$m, P6_3/mmc, and Pm$\bar{3}$n) and bicontinuous (Ia$\bar{3}$d and Pn$\bar{3}$m) pore structures obtained in silica mesoporous thin films. Reproduced with permission from Ref. Innocenzi et al. (2009)

and uncondensed materials (Falcaro and Innocenzi 2011; Innocenzi et al. 2012). When a mesostructured film containing gold precursors and templating micelles is exposed, just immediately after the deposition, to an X-ray beam through a mask, the X-ray induces the template removal, the condensation the inorganic pore walls, and the formation of gold nanoparticles into the pores. After this step, a chemical etching allows removal of the unexposed part of the film (Fig. 2), enabling the patterning. This approach has also the intrinsic advantage of writing thick hybrid films on a microscale in a short time (Falcaro et al. 2010).

The X-ray patterning method has shown to be highly flexible and has been applied to form gold (Innocenzi et al. 2011), silver (Malfatti et al. 2011), and even oxide nanoparticles, such as ceria (Pinna et al. 2013) into mesoporous ordered films. Patterned structures of different forms have been also produced via mask exposure and chemical etching. Another interesting possibility that has been explored is the fabrication of nanocomposite mesostructured films containing different guest active species, such as silver nanoparticles and graphene (Malfatti et al. 2016) (Fig. 3). In this case, graphene has been added in the precursor sol and the silver nitrate via post-production impregnation of titania-ordered mesoporous films. The exposure to X-rays promotes nucleation and growth of the silver nanoparticles, while it does not damage the graphene.

UV-Vis

Illumination of a mesoporous films by UV light is one of the most used methods to produce Ag NPs in mesoporous films. In general, the silver precursor, silver nitrate solution, is impregnated in the film pores or is introduced in the precursor sol. Illumination by UV light of the film allows reduction of the silver salt (Bois et al. 2010). To get an efficient reduction of the particles, photo sensitizers can be also employed (Eustis et al. 2006).

Patterned structures in the submicron scale of Ag NPs in titania mesoporous films have been obtained by exposing the films to UV light through a lithographic mask (Fig. 4) (Martínez et al. 2009).

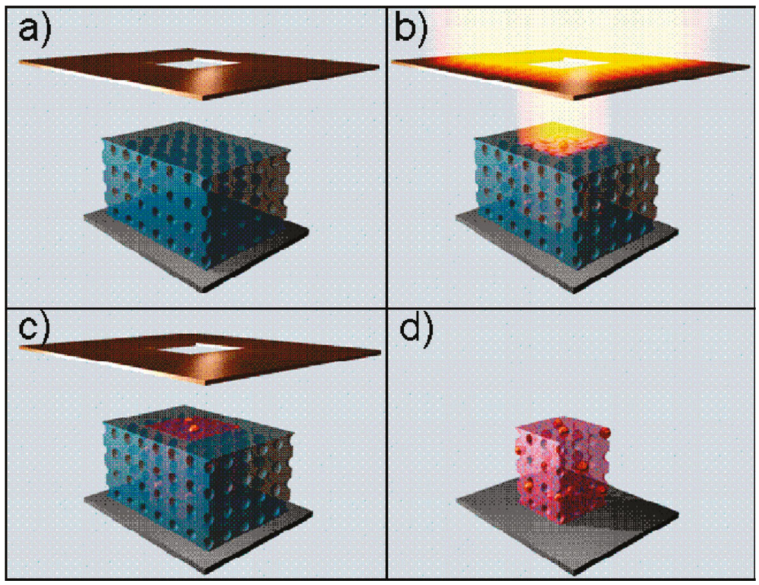

Fig. 2 Illustration of the X-rays lithographic process. **a** The mesostructured film containing the gold precursor and the templating micelles (**b**) is exposed just immediately after the deposition to an X-ray beam through a mask. **c** X-rays remove the template, condense the inorganic pore walls, and promote the formation of gold nanoparticles within the porous organized matrix of the film. **d** Chemical etching allows removal of the unexposed part of the film. Reproduced with permission from Ref. Innocenzi et al. (2011)

UV irradiation has been also used to form Pt NPs in silica 3D-Hex ($P6_3/mmc$) mesoporous films. The films have been deposited and dried under vacuum, then immersed into a platinum precursor solution. After a second drying step, the film has been irradiated by UV light (300–600 nm) to reduce H2PtCl6 to metallic Pt into the mesopores (Fig. 5). By this method NPs form also on the films surface and have to be removed by wiping (Kumai et al. 2006, 2010).

Laser irradiation

Irradiation with a monochromatic and focused light beam has been demonstrated to be an effective tool for microwriting mesoporous titania films with silver NPs (Crespo-Monteiro et al. 2010). The photogenerated electrons of titania reduce in fact the silver ions allowing the formation of silver nanoparticles. To produce the Ag NPs patterns, the mesoporous films, after their

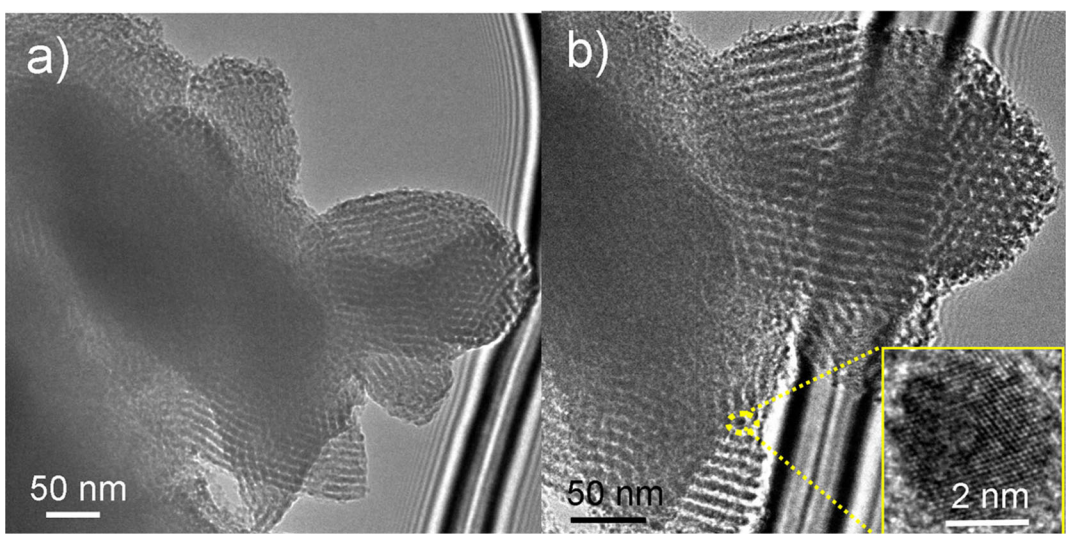

Fig. 3 **a** and **b** Bright-field TEM images of titania mesoporous films embedding exfoliated graphene (not visible) and crystalline Ag NPs (inset of **b**). Reproduced with permission from Ref. Pinna et al. (2013)

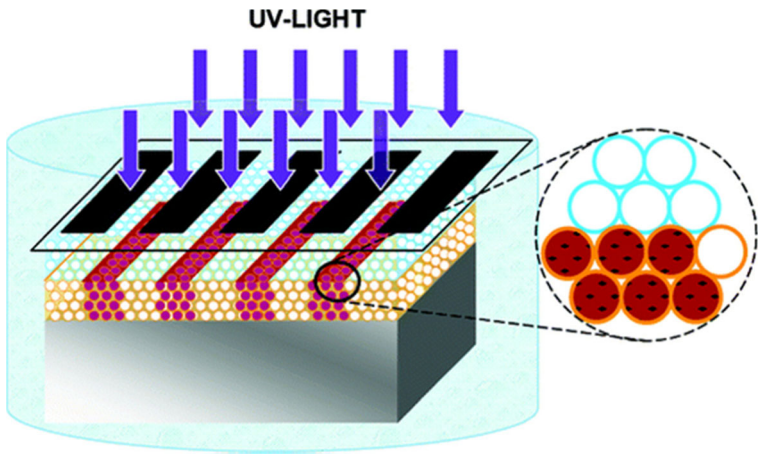

Fig. 4 The patterning process by UV light of a mesoporous titania films with Ag nanoparticles. Reprinted with permission from Ref. Eustis et al. (2006)

deposition, are immersed into an ammoniacal silver solution. The films have been then irradiated by a UV-laser using a CW doubled Ar laser (244 nm) or a HeCd laser (325 nm). These UV wavelengths are both absorbed by the TiO2 matrix triggering the formation of silver nanoparticles in the film. Laser irradiations in

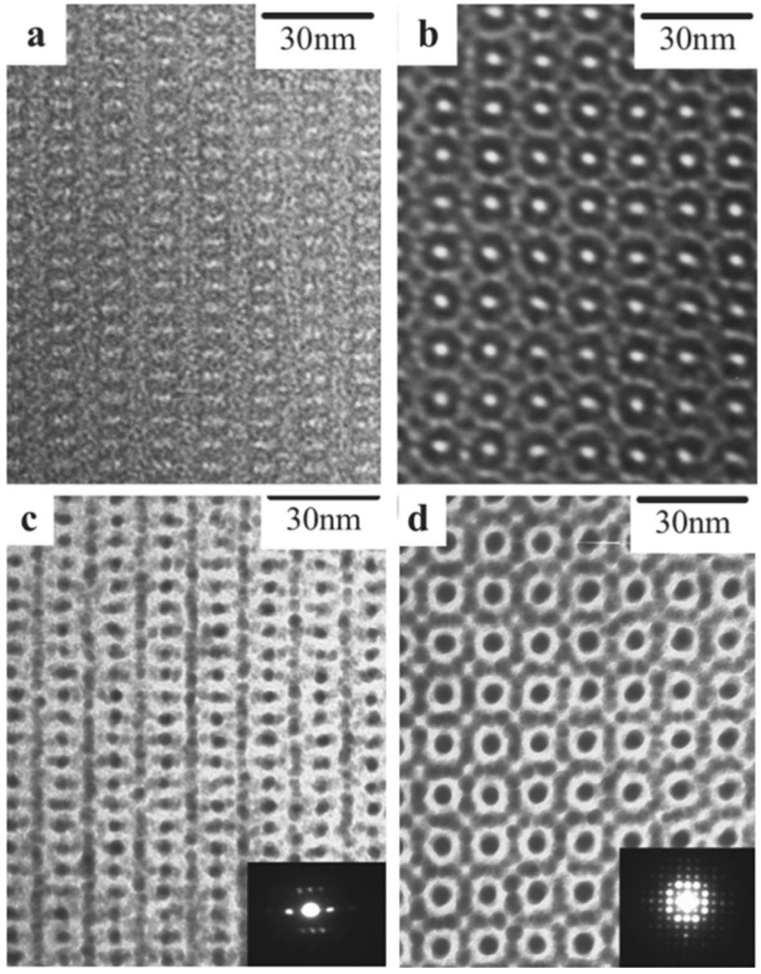

Fig. 5 **a** and **b** HRTEM images of mesoporous silica thin films before introduction of platinum. The regularly arranged, cage-like pores of the mesoporous silica thin film can be clearly observed. **c** and **d** HRTEM images of mesoporous silica thin films after introduction of platinum and their diffractograms. **a** and **c** [210] direction; **b** and **d** [100] direction. The HRTEM observation proves the extremely high quality of films with cubic symmetry and a 6.8-nm lattice constant. [210] and [100] incidences are observed clearly in the HRTEM images, and the size of the single-crystal-like domain is 200–350 nm. Reproduced with permission from Ref. Kumai et al. (2006)

the visible have been performed using a CW Ar laser emitting at 488 or 514 nm and a HeNe laser at 633 nm. The laser intensity has been adjusted by changing the focus of the laser beams or the output power, while to write the patterns an XY motorized stage has been used. Another interesting method of producing the nanoparticles in the irradiated area is two-beam laser interference lithography, which allows fabricating monodimensional (1D) gratings (Crespo-Monteiro et al. 2017). The mesoporous films have been at first exposed to UV light after impregnation with silver precursor solution and then homogeneously illuminated by UV light to form Ag NPs. After this step, the films have been patterned by laser interference to produce a microstructuration and a periodic distribution of Ag NPs close to the film surface.

Ion-beam deposition and atomic layer deposition

Ion beam deposition has proved to be a viable way to deposit nickel nanoparticles in the $Im\bar{3}m$ cubic mesopores of a silica film. By this method up ~30% of the total available cavities have been filled by the Ni NPs. After doping, carbon nanotubes have been grown by CVD (Acuña et al. 2010).

Layer deposition (ALD) has been used to form titania nanoparticles within mesoporous silica films. Alternating pulses of tetrakis(dimethylamino)titanium and water have allowed to deposited amorphous titania within the pores that upon calcinations transformed into anatase nanoparticles with a narrow size distribution. The system has shown a good photocatalytic activity as revealed by testing the photodegradation of methylene blue (Sree 2013).

Bottom-up routes

Chemical reductions

A simple and direct route to produce metal nanoparticles within the film mesopores is impregnation of the particle precursors within the pores followed by chemical reduction. One example is the formation of silver NPs into a mesoporous film by impregnation of an aqueous ammoniacal silver solution $[Ag(NH_3)_2]NO_3$ and the reduction obtained by immersing the film into a sodium borohydride ($NaBH_4$) aqueous solution (Chassagneux et al. 2011a, 2011b). The reduction of silver by $NaBH_4$ is quite fast, as shown by the film color change. Interestingly, in silica film, a change of the mesostructure during the reduction process has been observed. The change has been attributed to silver ion diffusion along preferential directions (Acuña et al. 2010).

Gold NPs into zirconia mesoporous film have been also produced by adsorption of a gold precursor ($HAuCl_4{\cdot}3H_2O$) followed by a reduction with $NaBH_4$ (Rodríguez et al. 2018). Controlling the pH of the doping solution is very important to allow the adsorption of the negatively charged Au(III) salt onto the positively charged surface of the film.

In general, to achieve an efficient adsorption of the precursor in silica mesoporous films, pre-functionalization of the surface by amine groups has to be performed (Calvo et al. 2010). 3-Aminopropyltriethoxysilane (APTES) (Fang et al. 2011) and N-[3(trimethoxysilyl)propyl]ethylene diamine (TPED) are some of the organosilanes, which have been used to modify the silica surface. The process employed for growing metal nanoparticles in silica mesoporous films is divided in two different steps (Fig. 6): surface modification and neutralization followed by thermal reduction (Gu et al. 2005). Another method to reduce metal ions in mesoporous silica films is the exposure to hydrazine (N_2H_4) vapor; silver, gold, and platinum NPs have been obtained by reduction of Ag^+, $AuCl^{4-}$, and $PtCl_6^{2-}$ ions (Dag et al. 2002). Chemical reduction has been also employed to produce Ag NPs arrays in a multilayer silica-titania system (Fuertes et al. 2009).

Thermal reduction

Thermal reduction of the precursor is another widely used method for producing metallic NPs (Innocenzi et al. 1994; Sayah et al. 2011) within the mesopores. It

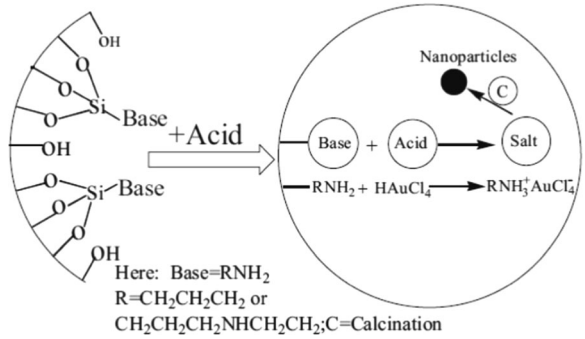

Fig. 6 Strategy to incorporate gold NPs into mesoporous ordered films. Reproduced with permission from Ref. Fang et al. (2011)

has the advantage that one-pot routes can be used avoiding several synthesis steps, but the thermal treatment can reduce the mesoporosity because temperatures higher than 300 °C are generally employed. Several examples of such synthesis have been reported for Ag (Ismail 2012) and Au nanoparticles in different matrixes. Homogeneous distribution of the particles within the matrix is very important, and several strategies have been employed to get a good dispersion of NPs with controlled size and shape. In general, multistep synthesis has been employed with surface modification and thermal reduction. An example is the use of (1,4)-bis(triethoxysilyl)propane tetrasulfide (BPTS) organosiloxane as coupling agent that, by co-reaction with tetraethylorthosilicate (TEOS), is used to produce mesoporous functionalized films. The synthesis is followed by oxidization, ion exchange with Au(1,2-ethanediamine)$_2$Cl$_3$, and calcination under hydrogen/nitrogen atmosphere (Gu et al. 2006). Thermal reduction in a controlled atmosphere, in Ar/H_2 or H_2/N_2 flows, is a very effective route to reduce metallic NPs, but it tends to modify also the oxide matrix, such as in titania mesoporous films (Zhang et al. 2008).

Impregnation-reduction processing is also viable for production of alloy NPs in mesoporous films (Zhang et al. 2008). One example is the formation of FeCo nanocrystals within silica mesoporous films through an impregnation process. The films have been at first impregnated with a solution containing Co(II) and Fe(III) ions and, after this step, the samples have been thermally treated under H_2 flow for the reduction and growth of the FeCo NPs (Costacurta et al. 2008).

Electrophoresis and electrical growth

Electrochemical reduction of precursors impregnated within the mesoporous films is an alternative way to obtain metallic nanoparticles. The film is deposited onto a conductive substrate which becomes the working electrode, and the application of an electrical potential allows metal NP formation. This method can be also used to obtain a metallic replica of the mesoporous structure of the film (Bannat et al. 2009; Wu et al. 2006). An interesting method to get a localized control of the NPs is the formation under a polarized microtip. A conductive tip of an atomic force microscope has been used to reduce the silver ions impregnated in a mesoporous silica film by a bias voltage between the tip and conductive substrate of tin oxide. The growth of Ag NPs has seen to be dependent on the bias voltage and the contact time (Hubert 2012).

Synthesis of mesoporous films containing semiconductor particles

The formation of semiconductor NPs in mesoporous films requires a different approach with respect to metal NPs. A number of examples have been reported for PbS (Buso et al. 2005), CdS (Besson et al. 2002; Qin et al. 2008), CdSe (Wark et al. 2002), or $Cd_{1-x}Mn_xS$ (Kouzema et al. 2004). In general, several syntheses have been designed for the different types of particles. In the case of PbS, two solutions containing the lead (lead acetate (Pb(CH3COO)2 3H2O)) and the sulfur precursor (thioacetamide (CH3-CSNH2)) have been used. The mesostructured films have been at first immersed into the lead acetate solution, to allow diffusing the lead, and later, after washing, immersed in the thioacedamide solution to form the PbS NPs, as indicated by the dark-brown coloration of the film. CdS and CdSe NPs in mesoporous films have been obtained by adding the Cd^{2+} ions into the sol and calcination at 623 K in a H2S or H2Se atmosphere. Core-shell PbS-CdS quantum dots have been introduced into mesoporous titania films via electrophoretic deposition (Lei et al. 2015) (Fig. 7).

The possibility to fabricate multicomponent nanocomposite mesoporous films is another example of the high flexibility of the synthesis through self-assembly. Many options are, in fact, offered to produce complex materials, which take advantage of the open and ordered porosity that represents an ideal host system for localized and controlled reactions. An example is the fabrication of CdS-Au systems in a mesoporous silica film (Qin et al. 2010). The nanocomposite has been obtained by a multistep process: impregnation by a methanol solution of cadmium acetate followed by a treatment in controlled atmosphere (5% H_2S in N_2) at room temperature to form the CdS NPs. Surface modification by APTMS to facilitate the adsorption of Au^+ ions introduced by dipping the film into an $AuCl_4$ solution. The last step is the immersion in a $NaBH_4$ solution to reduce gold and forming NPs. The final product is a mesoporous thin film containing CdS and Au NPs within the pores.

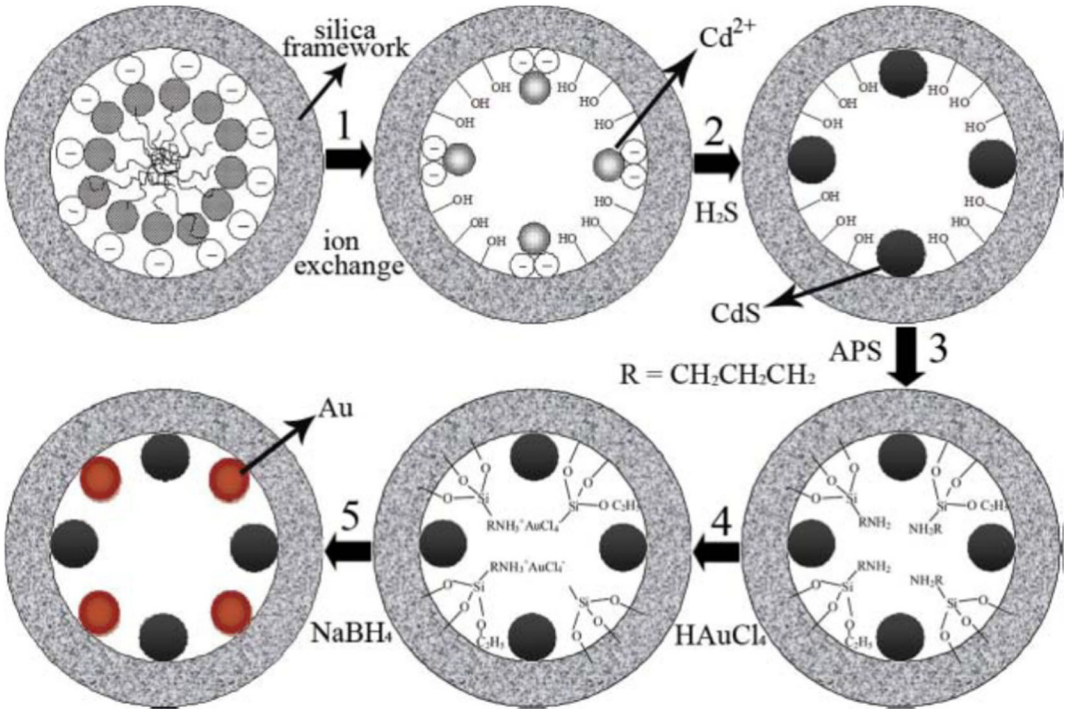

Fig. 7 Strategy used to form CdS-Au composites into the pore channels of mesoporous films. Step 1: first inner surface modification with Cd source; step 2: sulfidation to produce CdS NPs within the pores; step 3: second inner surface modification with 3-aminopropyltrimethoxysilane; step 4: neutralization reaction to introduce Au^{3+} into the pores; and step 5: reduction of Au^{3+} for the final CdS-Au NP-loaded mesoporous films. Reproduced with permission from Ref. Lei et al. (2015)

NPs in aligned mesochannels

Uniaxial alignment of mesochannels has been achieved via evaporation induced self-assembly using different synthesis methods (Miyata 2002; Miyata et al. 2015; Wu et al. 2011). The possibility of aligning the mesopores opens the route to important applications in photonics especially if the channels can be used to align plasmonic nanoparticles. Unidirectional aligned mesochannels parallel to the longitudinal axis has been used to obtain chain-like and spheroidal-like gold NPs in silica films (Fig. 8). The NPs have been formed by absorption of the gold precursors, reduction, and UV irradiation (Kawamura et al. 2012).

Another possibility is the formation of NPs in vertically oriented hexagonal mesoporous films (Richman et al. 2008). Gold NPs have been formed in silica mesopores aligned perpendicularly to an electrode surface (Ding et al. 2014). The surface has been modified with (3-aminopropyl)triethoxysilane to increase the electrostatic interaction with $AuCl_4^-$. After chemical reduction, the gold NPs resulted confined in the mesopores with a narrow size distribution.

Applications

The large porosity of the matrix, which has a high absorption capability and is the host of NPs with controlled shape and dimension, enables the development of different applications for mesoporous films.

Sensors

The adsorption capacity of mesoporous zirconia films and the electrocatalytic activity of gold NPs have been exploited for developing multifunctional electrodes; they have been tested for As(III) determination in aqueous solutions (Rodríguez et al. 2018). A chemical sensor based on the selective plasmonic response of phosphinine-stabilized gold nanoparticles hosted on mesoporous ordered silica films has been developed by Goettmann et al. (2005).

Disordered mesoporous WO_3 films containing with Pt NPs have been employed as ammonia gas sensors (D'Arienzo et al. 2011). The films under exposure to ammonia vapors have shown a significant electrical response, in particular at low NH_3 concentrations. This

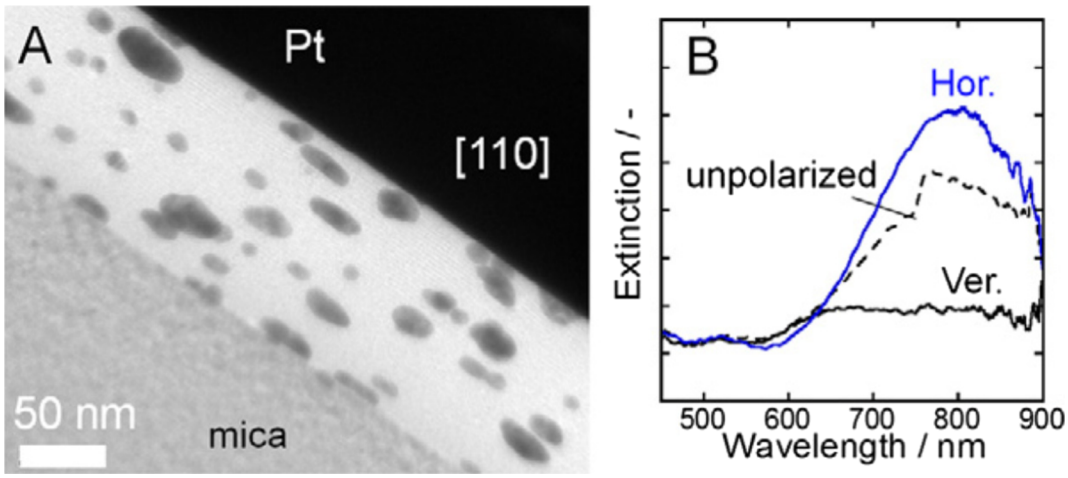

Fig. 8 **a** Cross-sectional TEM image of the Au-deposited SiO_2 film (UV irradiation) observed along the [110] zone axis of the mesoporous structure of the SiO_2 film. **b** UV-Vis spectra of the corresponding samples. Reproduced with permission from Ref. Wu et al. (2011)

response has been attributed to the cleavage of the N—H bonds by the Pt NPs inside the films that decreases the activation barrier of the ammonia dissociation.

Photocatalysis and catalysis

Mesoporous films whose oxide matrix is a semiconductor, such as titania, have been widely studied for photocatalysis. An improved photocatalytic effect under visible light has been observed in presence of metallic NPs, because the localized surface plasmon resonance band of the metallic NPs induces a higher absorption in the visible range. Several mesoporous-metallic NPs films have been therefore developed for this purpose. The photocatalytic activity of mesoporous titania films with Ag NPs has been tested using 2-chlorophenol degradation as a model reaction; the mesoporous films were eight times more effective than nonporous commercial photocatalytic glass (Sayah et al. 2011). An improved photocatalytic performance has been also observed in SiO_2-TiO_2-Ag NP system tested with methyl orange and methyl blue (Crespo-Monteiro et al. 2010). The mesoporous titania films with Ag NPs have also shown an increased bactericidal and sporocidal activity (Roldán 2014). Mesoporous titania films, containing gold NPs, have shown to perform a good photocatalytic oxidation of NO. The test has been realized by using two different types of samples, one with gold NPs formed by impregnation and chemical reduction, the other with electrochemical incorporation of dendritic gold structures. No differences have been observed in the performances even if the latter sample has the advantage of a simpler preparation. Interestingly, an additional O_2 plasma treatment improved the photocatalytic response because of the higher number of hydroxyls on the pore wall surface. Gold, silver, and platinum NPS in mesoporous titania and silica films have been also used for direct catalytic applications Cortial et al. (2006); NPs in the films have shown an increased activity in comparison to the bare particles.

An interesting application is free radical scavenging using ceria nanoparticles in titania mesoporous layers. The scavenging properties have been tested monitoring the UV photodegradation of rhodamine 6G. After impregnation with a rhodamine 6G solution, titania mesoporous films with and without ceria NPs have shown a different response upon exposure to UV light. The dye photodegradation is slowed down due to the antioxidant effect of ceria nanoparticles (Pinna et al. 2013).

Photonics

Incorporation of plasmonic particles into a dielectric matrix requires a good dispersion and control of NP dimension within the host film. Mesoporous ordered layers have been tested as potential candidates for developing nanocomposites with performing non-linear optical (NLO) properties.

Gold NPs in 2D hex (*p6mm*) mesoporous silica films have shown an ultrafast NLO response and enhanced third-order NLO susceptibility, $\chi^{(3)}$ (Fang et al. 2011, 2012). It has been observed an increase of $\chi^{(3)}$ with the gold content. An enhancement of $\chi^{(3)}$ is further obtained

upon incorporation of gold NPs into a high linear refractive index matrix such as titania (Cui 2009) or by magnetic field thermal treatment of the mesoporous films with the gold NPs (Cui et al. 2010a, 2010b). A significant $\chi^{(3)}$ increase has been also observed in mesoporous silica film containing Ag NPs Lu et al. (2011), with a measured value which has been 1000 times larger than Ag NP chalcogenide glasses (Tan and Liu 2016; Gu et al. 2009). Magnetic field-induced off-resonance third-order optical nonlinearity has been also observed in mesoporous silica thin films containing iron oxide nanoparticles (Andreou et al. 2013). The origin of the NLO response has been attributed to the magnetic domain orientation of the iron oxide NPs induced by a specific magnetic field treatment.

Mesoporous films with NLO response have been also prepared using semiconductor nanoparticles. Silica mesoporous films with lead sulfide NPs have shown a quantum confinement effect, revealed by a blue shift of the optical absorption edge with respect to the bulk PbS and a high third-order optical non-linearity (Wu et al. 2006). Enhanced susceptibility has been also measured in mesoporous films with CdS NPs (Besson et al. 2002) and in CdS-Au nanocomposites (Lei et al. 2015). The multicomponent NPs have shown, in particular, an enhanced third-order NLO susceptibility at 1064 nm in comparison to the single component samples. This enhancement has been attributed to the energy transfer between CdS and Au and to the uniform size and high dispersion of CdS and Au NPs, which are confined in the mesopores.

Surface-enhanced Raman scattering

Surface-enhanced Raman scattering (SERS) is an analytical method based on the enhancement of the sensitivity of Raman scattering by the plasmons of metallic NPs and metallic rough surfaces. The technique can be very sensitive reaching a single-molecule detection (Cui et al. 2010a, 2010b). Mesoporous materials containing SERS active Ag and Au NPs are an interesting platform to develop selective and highly sensitive sensors. A first example has been reported by Malfatti et al. who prepared mesoporous silica ordered film with Ag NPs as a lab-on-chip SERS detection surface for rhodamine 6G (Malfatti et al. 2011). An advantage of using mesoporous films as platform for SERS is the large surface area available for analyte detection and the possibility to play with sol-gel chemistry by designing a matrix which is able to select the analyte, for instance via molecular imprinting (Carboni et al. 2016). Titania and zirconia mesoporous films containing Ag NPs have been also tested to detect 4-mercaptopyridine as a probing molecule, while bilayer mesoporous structures have shown to provide additional control on the analyte selectivity (Wolosiuk et al. 2014). The possibility of changing the pore surface by functional groups, which have a specific chemical affinity, is an alternative route to develop selective sensors. Amino-functionalized hybrid mesoporous thin films with Ag NPs have been used for selective detection of methylene blue (Lopez-Puente et al. 2015). Mesoporous thin films offer also an interesting possibility of hot-spot engineering for SERS substrates (Wang et al. 2016). Gold NPs have been anchored on vertically aligned silica mesoporous films to obtain a precise distance (around 2 nm) between the NPs (Fig. 9). This array has shown to enhance the local electric field and form a SERS substrate with uniform response.

Anisotropic gold NPs in mesoporous γ-Al_2O_3 films have shown SERS activity and strong absorption in the near IR region because of the peculiar particle morphology (Dandapat et al. 2013).

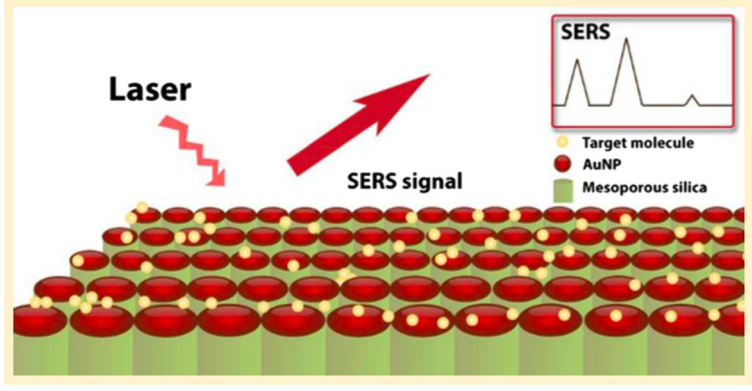

Fig. 9 A SERS platform with gold nanoparticles regularly anchored on the top of vertically aligned mesoporous channels. Reprinted with permission from Ref. Wang et al. (2016)

Photochromism

Photochromism of silver NPs in titania mesoporous films has been used to obtain writable-erasable substrates for laser inscription. Monochromatic visible light, in fact, can produce oxidation of Ag nanoparticles and erase a UV-printed pattern. Below the intensity threshold, UV and visible radiations, respectively, have been used for a cycle of writing-erasing of yellow-brown micropatterns, demonstrating the fully rewritable character of the films. Exposure to continuous wave (CW) laser has produced a surface change on titania mesoporous films due to local crystallization, and this effect has been used to form non-erasable micropatterns (Martínez et al. 2009).

A future outlook

The synthesis via self-assembly of mesoporous films with ordered and controlled porosity can be actually considered a well-established field. Material composition and pore topology design can be achieved with a reasonable degree of accuracy and oxides, and hybrid organic-inorganic matrixes give a wide choice of possible options for developing functional applications. The present challenge is adding an active function to the mesoporous films for fabricating advanced working devices. Nanocomposites based on mesoporous films and NPs are an interesting field of application, and several solutions have been already proposed. Most of the materials are however based on silver and gold nanoparticles, while relatively few examples are reported for other metals, semiconductors, and oxides. One of the main advantages of mesoporous materials, beside the high surface area and the organized porosity is the possibility of surface functionalization which in some cases, such as sensing, can be an added value for the performance of the sensor. In the next future, some new and unexpected applications based on the combined properties of mesoporous film and nanoparticles will be likely to appear.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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