Anales de la Asociación Química Argentina

División Jóvenes Profesionales

Mini-Review

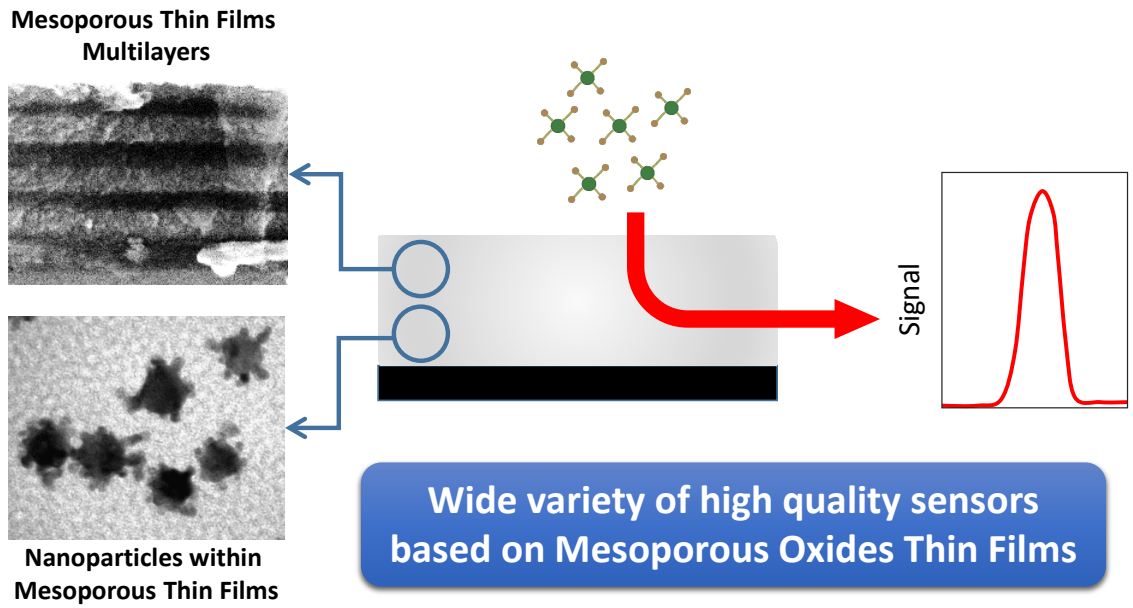
MESOPOROUS THIN FILMS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN SENSING

M. Mercedes Zalduendo, Josefina Morrone, Paula Y. Steinberg, M. Cecilia Fuertes, Paula C. Angelomé*

Gerencia Química & Instituto de Nanociencia y Nanotecnología, CAC-CNEA, CONICET. Avenida General Paz 1499, B1650KNA, San Martín, Buenos Aires, Argentina

**Autor Corresponsal: angelome@cnea.gov.ar*

Graphical abstract



Resumen

Las películas delgadas de óxidos mesoporosos (PDOMPs) han recibido mucha atención en las últimas décadas, principalmente debido a su arreglo controlado de poros con diámetro en el rango 2 - 50 nm y su versatilidad para el desarrollo de dispositivos tecnológicos. Hoy en día, se encuentran disponibles diversos moldes de poros y precursores inorgánicos lo que permite obtener una gran variedad de PDOMPs tanto en términos de composición química (SiO_2, TiO_2, ZrO_2, CeO_2, $Al2O_3$, HfO_2 y óxidos mixtos) como de tamaños y arreglos de poros. Entre las aplicaciones propuestas para las PDOMPs, una de las más destacadas es su uso como parte constitutiva de sensores. Las principales ventajas de usar PDOMPs en la construcción de estos dispositivos son: la alta superficie específica, la versatilidad de composición química y la facilidad para depositarlas sobre una gran variedad de sustratos.

En este trabajo de revisión se describen brevemente los métodos de síntesis más usuales para obtener PDOMPs y las técnicas de caracterización más utilizadas para determinar sus

propiedades fisicoquímicas. Posteriormente, se analizan dos de las líneas que se están desarrollando en nuestro grupo para obtener sensores específicos y reproducibles basados en PDOMPs: sensores para espectroscopía Raman aumentada por superficies (SERS) obtenidos al combinar las películas con nanopartículas metálicas y sensores ópticos basados en multicapas.

Abstract

Mesoporous oxide thin films (MOTFs) have received much attention in the last decades mainly because of their controlled array of pores with diameter in the 2-50 nm range and their versatility for development of technological devices. Nowadays, a diversity of pore templates as well as inorganic precursors are available, therefore a large variety of MOTFs can be obtained in terms of chemical composition (SiO_2, TiO_2, ZrO_2, CeO_2, Al_2O_3, HfO_2, and mixed oxides) and pore sizes and arrangements. Among all the proposed applications of MOTFs, one of the most prominent is their use as constitutive part of sensors. The main advantages of using MOTFs in the construction of these devices are: high specific surface, chemical composition versatility and the easiness to deposit them onto a wide variety of substrates.

In this minireview, we shortly describe the most common synthesis methods to obtain MOTFs along with the most usual techniques used to characterize their physicochemical properties. Afterwards, we discuss two of the lines that are being developed in our group to obtain specific and reproducible sensors based on MOTFs: Surface Enhanced Raman Spectroscopy (SERS) sensors obtained by combining the films with metallic nanoparticles and optical sensors based on films multilayers.

Palabras Clave: *películas delgadas, óxidos mesoporosos, nanopartículas metálicas, multicapas, sensores*

Keywords: *thin films, mesoporous oxides, metal nanoparticles, multilayers, sensors*

.

1. Introduction

Mesoporous oxide thin films (MOTFs) have received much attention in the last decades mainly due to their high surface area and versatility for development of technological devices.[1-2] Mesopores dimensions (2-50 nm diameter)[3] give place to confinement effects which are crucial in catalysis, nanoreactors, nanofluidics and diffusion.[4-8] At the same time, these materials are able to interact with larger molecules than in the case of other (micro)porous materials, such as proteins, polymers and nanoparticles.[9-12]

Typical ways to obtain thin films are by dip-coating or spin-coating a precursor solution onto different substrates such as glass, silicon, gold, quartz or conductive glass (ITO, FTO). Some parameters as withdrawal or spin speed and solution viscosity allow tuning films thickness; and other parameters as ambient humidity and temperature have critical effect on pores spatial

organization and films optical quality.[13-14] Although less utilized, other deposition methods are also applied: spray-coating, casting, convective self-assembly and electrochemical assisted deposition.[1] During and after deposition, two processes take place: evaporation induced self-assembly of amphiphilic molecules that form micelles, which work as pores template, and sol-gel reactions, that form the oxide around the micelles.[15-18] Afterwards, samples are treated at moderate or high temperature (200-700°C)[1-2] or with X-rays (2.5-12 keV)[19] to eliminate the pore template and to yield oxide consolidation and even its crystallization. Furthermore, this synthetic methodology permits the addition of other chemical moieties by co-condensation or post-grafting[11, 20-21], and/or the incorporation of metal or semiconducting nanoparticles.[10, 22-23] Thus, a large variety of designs can be achieved.

The resulting MOTFs are defined by their thickness, refractive index, pore size, pore spatial distribution, pore accessibility, wall crystallinity and mechanical properties. All these features can be fully characterized by using several complementary techniques.[1-2, 14] In general pore size and its spatial distribution are obtained by means of scanning and transmission electron microscopy (Figure 1A-C), and grazing incident small angle X-ray scattering (Figure 1D). Inorganic or organic chemical composition is determined with optical spectroscopies such as UV-visible, FTIR and Raman.[14, 24] Wall crystallinity can be verified by X-ray diffraction, selected area electron diffraction, Raman spectroscopy and even X-ray absorption methods.[14, 24-26] To obtain information about porosity, thickness and refractive index, X-ray reflectometry (Figure 1E) and environmental ellipsometric porosimetry (EEP, Figure 1F) are carried out.[27-28] Either EEP or nanoindentation provide MOTFs mechanical properties.[24] In some cases, *in situ* studies are possible and permit to follow films evolution throughout the thermal treatment.[14, 29-32]

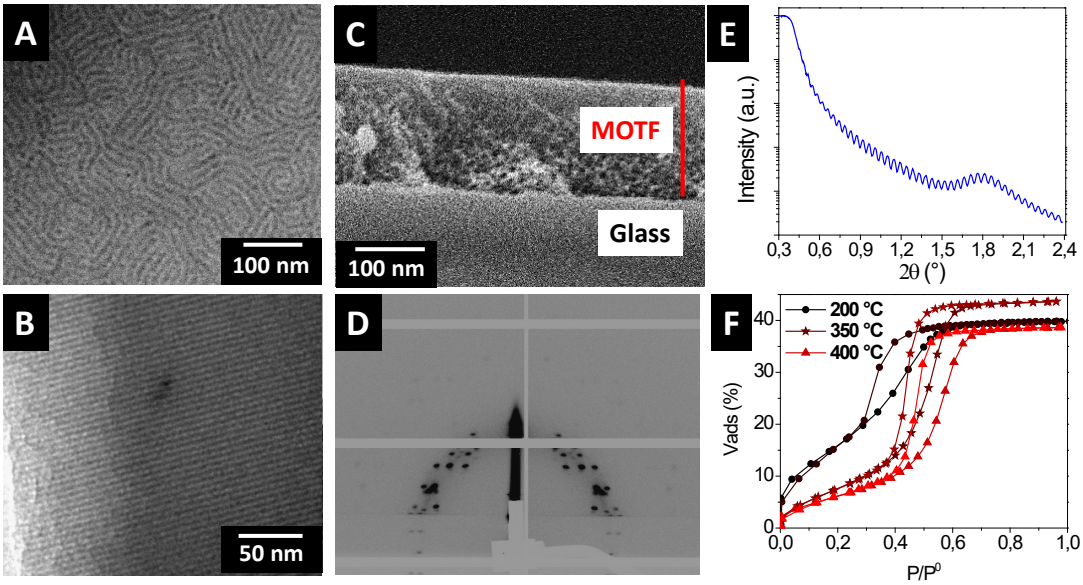


Figure 1. (A) SEM image of a mesoporous SiO_2 thin film templated with Pluronic F127 and treated at 350°C. (B) TEM image of a mesoporous SiO_2 thin film templated with Brij 58 and treated with X-rays. (C) SEM side view of a mesoporous TiO_2 thin film templated with Pluronic P123 and treated at 350°C. (D) GISAXS pattern of a SiO_2 thin film templated with CTAB deposited on silicon and treated with X-rays. (E) X-ray reflectogram of a TiO_2 thin film templated with Pluronic F127 deposited on glass and treated at 350°C. (F) Water adsorption-desorption isotherms of TiO_2 thin films templated with Brij 58 deposited on ITO and treated at 200, 350 and 400°C.

The development of MOTFs was possible thanks to the detailed characterization of each synthesis step and the complete description of the final material´s properties. Nowadays, a diversity of pore templates as well as inorganic precursors are available, therefore a large variety of MOTFs can be obtained in terms of chemical composition (SiO_2, TiO_2, ZrO_2, CeO_2, Al_2O_3, HfO_2, and mixed oxides) and pore sizes and distribution (*Pm3n* as in Figure 1D, *Im3m* as in Figure 1A-B, *Fm3m* as in Figure 1C, 2D-hexagonal, 3D-hexagonal).[14, 30, 33-36] The possibility of combining the MOTF with NPs and/or inorganic/organic/biological compounds opens endless potential applications.[1]

Among all the proposed applications of MOTFs, one of the most prominent is their use as constitutive part of sensors. The main advantages of using MOTFs in the construction of these

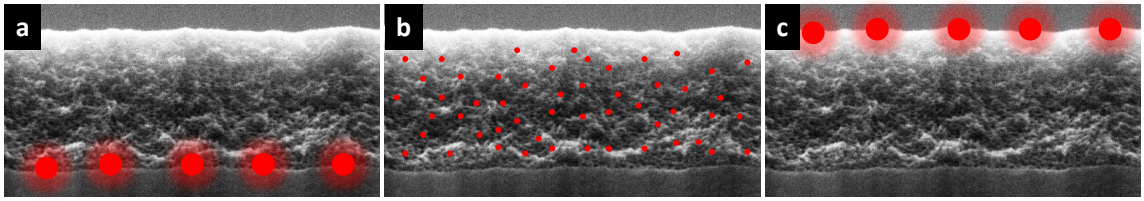
devices are their high specific surface, their chemical composition versatility and the easiness to deposit them onto a wide variety of substrates. Several examples were presented regarding the applications of MOTFs: single layers of hybrid MOTFs were tested as optical sensors, [37-39] while silica mesoporous films were applied for humidity and vapor sensing.[40-47] Moreover, improvement on specificity and selective sensing can be envisioned when increasing the complexity of the devices, either by combining several MOTFs or by adding other nanomaterials or functions in their structure. In the following sections, we will discuss two of the lines that are being developed in our group to obtain specific and reproducible high complexity sensors based on MOTFs: Surface Enhanced Raman Spectroscopy (SERS) sensors obtained by combining films with metallic nanoparticles and optical sensors based on films' multilayers.

2. SERS based sensors

MOTFs can be combined with metal nanoparticles to build a new material with distinctive optical properties.[10, 22-23] MOTFs represent a good alternative for nanoparticles (NPs) support and stabilization, where the large surface area ensures direct contact between the NPs and the environment. Consequently, these platforms had found applications as optical sensors. In particular as SERS based sensors,[48-52] where the MOTFs plays an active role not only generating the enhancement platform but also providing specificity to the detection.[53-58] In this line, the sensor´s performance, affinity and selectivity can be tuned modifying the MOTF pore size, charge and/or functionalization.

Diverse soft chemistry and/or lithography techniques approaches can be used to join MOTFs and metal NPs in a new material.[10, 22-23] The different synthetic pathways will define the material´s final configuration. Some of the proposed architectures are presented in Scheme 1: (a) metal NPs can be placed between the substrate and the film (Architecture 1) or (c) above the film in the air-MOTF interface (Architecture 3). Other possibility is the synthesis of the metal NPs inside the

pores or at the walls of the porous film (Architecture 2, Scheme 1b). In all cases, the main features of the MOTF are not altered by the incorporation of the metal NPs.



Scheme 1. Schematic representation of possible architectures built by combining metal NPs and MOTF: (a) MOTF deposited on a substrate with immobilized metal NPs; (b) metal NPs synthesized in the pores or at the walls of the MOTF; and (c) metal NPs deposited above the MOTF.

Figure 2 displays electronic microscopy images of different samples with the already described architectures. Figures 2a, b and c represent examples of Architecture 1. NPs of different morphologies (triangles, rods and spheres) were immobilized and coated with a MOTF (Figures 2a, b and c, respectively).[53, 56, 59] More anisotropic shapes can be obtained by NPs overgrowth through the pores of the film that covers them (Figure 2d).[56, 60] In fact, this last feature demonstrates, in a simple way, the accessibility of the MOTF since molecules (in this case, reaction precursors) can diffuse from solution to the bottom of the film, where the NPs are placed. On the other hand, Figures 2e and f are examples of Architecture 2. Gold NPs were synthesized inside the pores of the MOTF and are evenly distributed through the film´s thickness, as can be seen from the SEM cross-section image in Figure 2f.[56, 61]

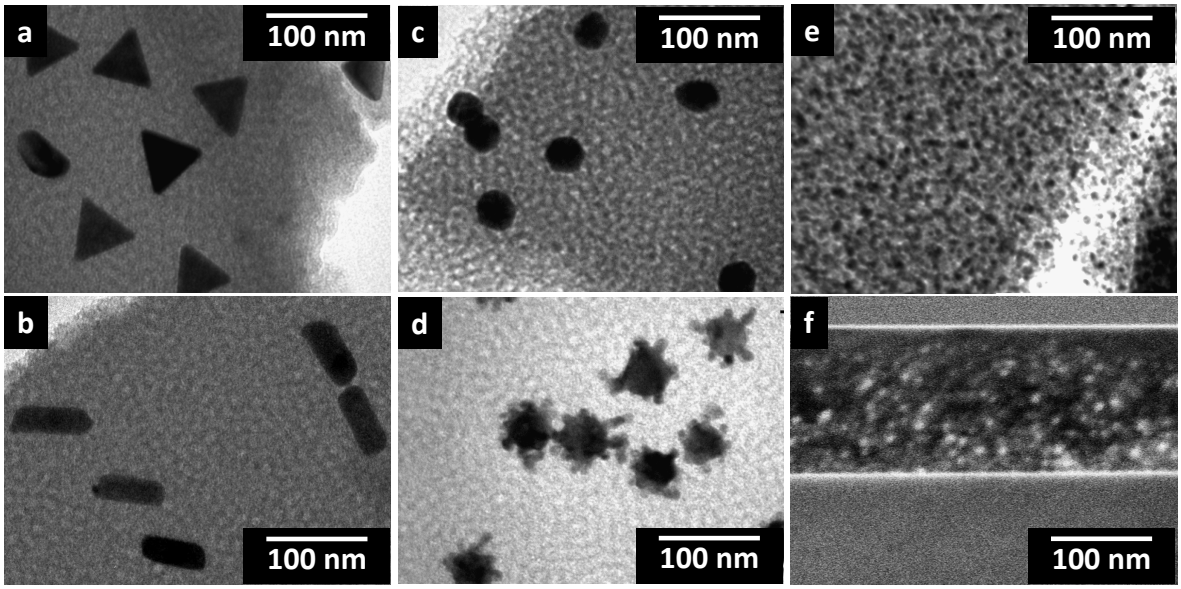


Figure 2. TEM images of: (a) Au nanotriangles, (b) Au nanorod, and (c) Au spherical NPs of 35nm diameter covered with mesoporous TiO_2. (d) TEM image of overgrown Au 35nm diameter spherical NPs. (e) TEM image and (f) SEM cross-section image of Au NPs synthesized inside a TiO_2 mesoporous film.

The final material´s optical properties and sensing capabilities are intrinsically related to its architecture. As an example, Figure 3 shows the SERS intensity of a probe molecule as a function of spatial coordinates, for three different platforms. Panels (a) and (b) correspond to an Architecture 1 type: aggregated 66 nm diameter Au NPs and overgrown isolated Au 66 nm NPs coated with MOTF, respectively. In both cases, a large number of hot spots are formed, given by NPs proximity and the presence of tips in the overgrown NPs.[62-63] Therefore, high SERS intensity is detected. On the other hand, Figure 3c exhibits the SERS performance of a type 2 architecture: Au NPs were synthesized in the pores of a MOTF. Low intensity signal is observed due to the small size of the NPs, limited by pore diameter.[56] However, since NPs are evenly distributed in the three directions of the ordered MOTF, a high signal spatial distribution (usually difficult to obtain through other soft chemistry techniques) is identified. As a general result, high SERS signals are obtained with Architecture 1 sensors while high spatial homogeneity is obtained with architecture 2 devices.[54, 56] Therefore, the choice of one sensing platform over another will depend on the envisioned application. In particular, highly homogeneous type 2 architectures are ideal for routine determination of analytes that are present in μM

concentrations. Highly sensitive type 1 architectures, on the other hand, are ideal in case filtering or high sensitivity are needed.[53, 64]

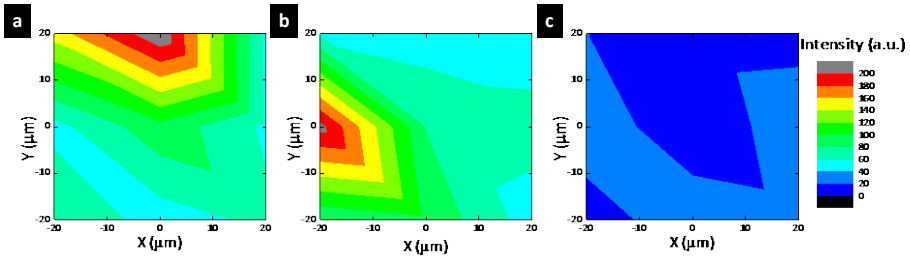


Figure 3. SERS maps of p-nitrothiophenol 1340 cm^{-1} band intensity for different samples: (a) aggregated Au 66nm NPs coated with mesoporous TiO_2, (b) overgrown isolated Au 66nm NPs covered with mesoporous TiO_2, and (c) Au NPs synthesized inside the pores of mesoporous TiO_2.

In summary, a great variety of architectures can be obtained combining metal NPs and MOTFs. The features of each component remain in the new material while additional properties arise from their association. Each architecture presents different optical properties, therefore, distinctive sensing capabilities.

3. Optical sensors based on multilayered structures

Thin films alternated layers of low/high refractive index lead to obtain one dimension photonic crystals (PC), commonly known as Distributed Bragg Reflector (DBR).[65] If these arrangements are porous, they can be used as optical sensors in both liquid and vapour phase. PC based sensors respond to changes in the medium's refractive index by a shift in the photonic band gap; therefore, it is possible to evidence changes in the environment by a colour variation.[66-70] In a further step, the sensitivity of the sensor can be increased by depositing a noble metal thin film next to the higher refractive index layer; generating the recently experimentally developed Tamm mode.[71-75] Such feature is expected to enhance the sensitivity due to the thinner spectral band that these optical modes present, when compared to the DBR ones.[75]

Mesoporous PC based sensors are mainly obtained by soft chemistry methods using as precursors oxides nanoparticles suspensions[76-80] or sol-gel solutions[75, 81-89] to prepare each

MOTF layer. If a Tamm mode based sensor is desired, the thin layer of the noble metal can be either sputtered on top of the multi-layered structure or can be deposited onto the substrate and covered by the DBR. These two possible architectures are depicted in Figure 4, together with a detailed image of the porous multilayer and an optical image of one device.

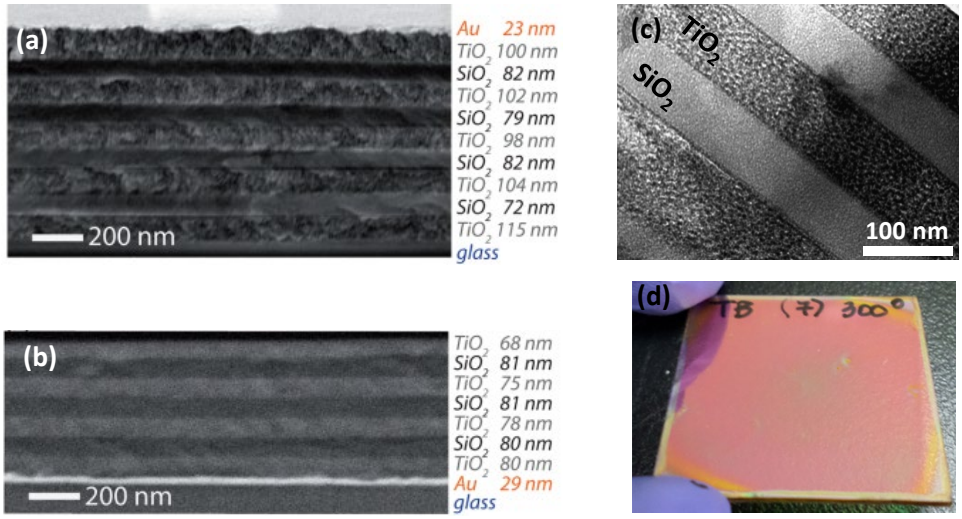


Figure 4. SEM images and the corresponding schemes of two possible architectures for a Tamm device: (a) DBR deposited on a glass substrate with a gold layer on top; (b) DBR deposited on a gold coated glass substrate. Reprinted with permission from [75]. Copyright 2014 American Chemical Society. (c) TEM image showing the porous structure of the mesoporous layers and (d) optical image of a Tamm device prepared on glass.

The performance of these sensors is evaluated measuring the variation of the minimum (for the Tamm device[75]) or the maximum (for the PCs based sensors[76-77, 81-82]) of the photonic band gap as a function of the stimulus (*i.e.* vapor concentration, liquid refractive index, etc). The sensitivity and selectivity of the multi-layered materials can be tailored by modifying the physicochemical nature of the MOTFs that forms the device. The chemical modification can be achieved by one-pot co-condensation during the synthesis of the layers, or by post-grafting, either by complexing or forming covalent bonds.[20] An example of the versatility of such chemical modification has been present by Ghazzal *et al.* These authors studied the selectivity of PCs based on alternated titania and silica mesoporous films by changing the ratio of hydrophobic function of the silica layers by one-pot co-condensation.[85] To evaluate the performance, they

exposed the devices to solvents with different hydrophilic behaviour (water or hexane). Figure 5a shows the spectral response of the PC when it is exposed to the solvents, meanwhile the Figure 5b shows the variation of the band gap position as function of the hydrophobic component ratio. It can be observed that as the hydrophobic function content increases, the diffusion of water inside the layers becomes more difficult due to the surface affinity.

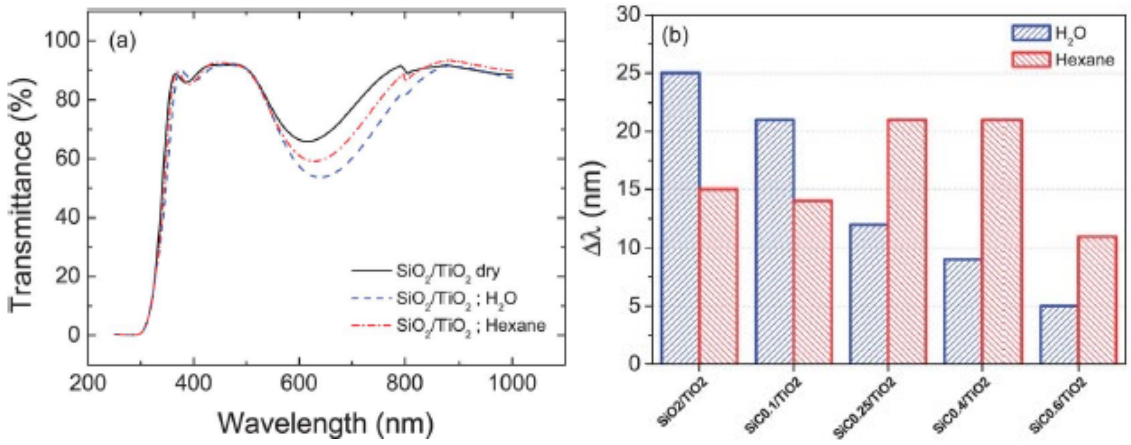


Figure 5. (a) Spectral response of a dry PC (black), and when it is exposed to water (blue) and hexane (red). (b) Band gap shift of the photonic crystal as function of the hydrophobic function and the solvent. Reproduced from Ref. [85] with permission from The Royal Society of Chemistry.

Our group has already tested the Tamm devices as optical sensors, proving the response from changes in the environment and opening the path to develop this type of devices.[75] As an example, in Figure 6 the response of two different Tamm devices as toluene detectors is shown, in both liquid (Figure 6a) and vapour (Figure 6b) phases. In a continuation of this work, we have demonstrated the higher sensitivity of these sensors versus those based on PCs. It was also shown that the response of this sensors not only depends on the nature of the device, but also on the physicochemical properties of the solvents, such as polarity or vapour pressure.[90]

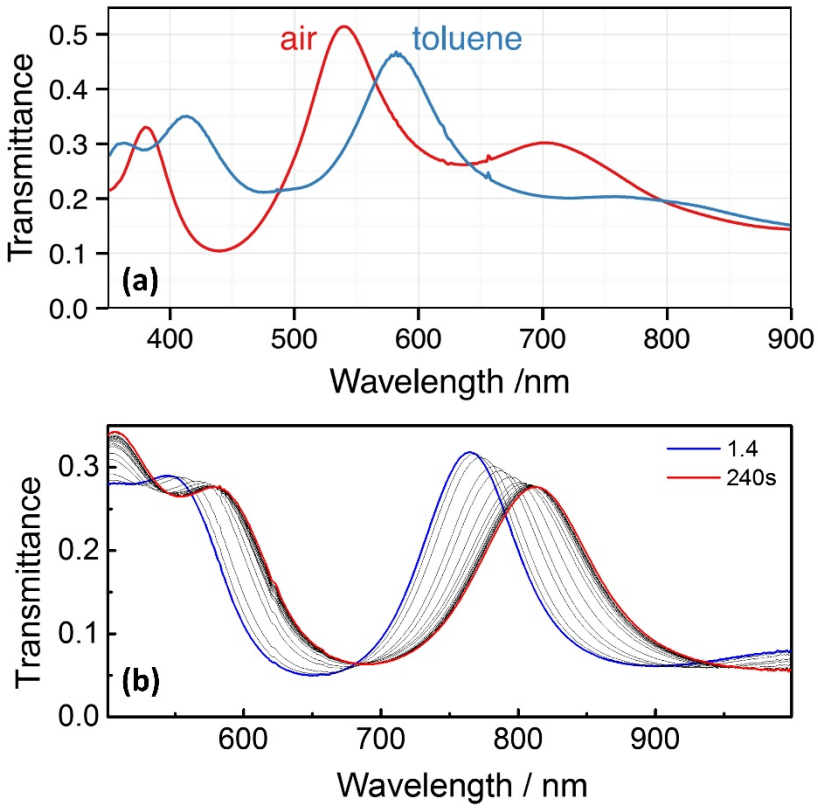


Figure 6. (a) Experimental transmittance spectra of a Tamm device exposed to air (red line) and after immersion in liquid toluene (blue line). Reprinted with permission from [75]. Copyright 2014 American Chemical Society. (b) Spectral response of a dry Tamm device (blue) when it is exposed to toluene vapors, until the condensation of liquid toluene inside the pores is reached at 240 s (red).

In summary, mesoporous PC based sensors, both DBR and Tamm devices, were proved to be good as vapour and liquid detectors. It has also been shown that the features of the materials can be modified with accessible reactions, which do not require a difficult work-up. Therefore, the simple design and construction method allows producing sensors on demand, and the combination of them makes possible obtaining photonic noses arrays.[91-92]

4. Conclusions

MOFTs are very versatile materials, whose physicochemical and structural characteristics can be designed and tuned from synthesis. Thus, their use as constitutive part of sensors is straightforward. Moreover, if the films are stacked or combined with other nanomaterials,

multiple variety of architectures can be obtained, with new properties that depend on the components' physicochemical features and position. Consequently, more complex and specific sensors are expected to be built in such approach. In this minireview, we have demonstrated that MOTFs can be combined with metallic nanoparticles to obtain highly sensitive SERS based sensors with architecture dependent performance. In the same way, we have shown that DBRs based optical sensors can be prepared by stacking MOTFs and the sensitivity of the device can be tuned by taking advantage of the films' functionalization. The selected cases are just a small sample of MOTF based sensing possibilities. Other applications are currently under development worldwide, and much more examples are expected to be available in the near future.

Acknowledgments:

M.M.Z, J.M. and P.Y.S. acknowledge CONICET for their doctoral fellowships. Financial support from ANPCyT (PICT 2015-0351) and CONICET (PIP 2012-00044CO) is gratefully acknowledged.

References

(1) Innocenzi, P.; Malfatti, L., Mesoporous thin films: properties and applications. Chem. Soc. Rev. **2013**, 42 (9), 4198-4216.
(2) Soler-Illia, G. J. A. A.; Angelomé, P. C.; Fuertes, M. C.; Grosso, D.; Boissière, C., Critical aspects in the production of periodically ordered mesoporous titania thin films. Nanoscale **2012**, 4 (8), 2549-66.
(3) IUPAC, Manual of Symbols and Terminology. Pure Appl. Chem. **1972**, 31, 578.
(4) Perego, C.; Millini, R., Porous materials in catalysis: challenges for mesoporous materials. Chem. Soc. Rev. **2013**, 42 (9), 3956-3976.
(5) Kärger, J., Transport Phenomena in Nanoporous Materials. ChemPhysChem **2015**, 16 (1), 24-51.
(6) Michaelis, J.; Bräuchle, C., Reporters in the nanoworld: diffusion of single molecules in mesoporous materials. Chem. Soc. Rev. **2010**, 39 (12), 4731-40.
(7) Polarz, S.; Kuschel, A., Chemistry in confining reaction fields with special emphasis on nanoporous materials. Chemistry 2008, 14 (32), 9816-29.
(8) Schoch, R. B.; Han, J.; Renaud, P., Transport phenomena in nanofluidics. Rev. Mod. Phys. **2008**, 80 (3), 839-883.
(9) Moller, K.; Bein, T., Mesoporosity - a new dimension for zeolites. Chem. Soc. Rev. **2013**, 42 (9), 3689-3707.
(10) Angelomé, P. C.; Liz-Marzán, L. M., Synthesis and applications of mesoporous nanocomposites containing metal nanoparticles. Journal of Sol-Gel Science and Technology **2014**, 70 (2), 180-190.
(11) Alberti, S.; Soler-Illia, G. J. A. A.; Azzaroni, O., Gated supramolecular chemistry in hybrid mesoporous silica nanoarchitectures: controlled delivery and molecular transport in response to chemical, physical and biological stimuli. Chem. Commun. **2015**, 51 (28), 6050-6075.
(12) Soler-Illia, G. J. A. A.; Azzaroni, O., Multifunctional hybrids by combining ordered mesoporous materials and macromolecular building blocks. Chem. Soc. Rev. **2011**, 40 (2), 1107-1150.
(13) Grosso, D., How to exploit the full potential of the dip-coating process to better control film formation. Journal of Materials Chemistry **2011**, 21 (43), 17033.
(14) Crepaldi, E. L.; Soler-Illia, G. J. d. A. A.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C., Controlled Formation of Highly Organized Mesoporous Titania Thin Films: From Mesostructured Hybrids to Mesoporous Nanoanatase TiO2. Journal of the American Chemical Society **2003**, 125 (32), 9770-9786.
(15) Brinker, C. J.; Hurd, A. J.; Schunk, P. R.; Frye, G. C.; Ashley, C. S., Review of sol-gel thin film formation. Journal of Non-Crystalline Solids **1992**, 148, 424-436.

(16) Tang, Q.; Angelomé, P. C.; Soler-Illia, G. J. A. A.; Muller, M., Formation of ordered mesostructured TiO2 thin films: a soft coarse-grained simulation study. Phys. Chem. Chem. Phys. **2017**, 19 (41), 28249-28262.
(17) Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C., Block copolymer-templated mesoporous oxides. Curr. Opin. Colloid Interface Sci. **2003**, 8 (1), 109-126.
(18) Tarutani, N.; Tokudome, Y.; Jobbágy, M.; Soler-Illia, G. J. A. A.; Takahashi, M., Mesoporous microspheres of nickel-based layered hydroxides by aerosol-assisted self-assembly using crystalline nano-building blocks. Journal of Sol-Gel Science and Technology **2018**.
(19) Innocenzi, P.; Malfatti, L.; Marmiroli, B.; Falcaro, P., Hard X-rays and soft-matter: processing of sol–gel films from a top down route. Journal of Sol-Gel Science and Technology **2013**, 70 (2), 236-244.
(20) Nicole, L.; Boissiere, C.; Grosso, D.; Quach, A.; Sanchez, C., Mesostructured hybrid organic-inorganic thin films. Journal of Materials Chemistry **2005**, 15 (35-36), 3598-3627.
(21) Soler-Illia, G. J. A. A.; Innocenzi, P., Mesoporous hybrid thin films: The physics and chemistry beneath. Chemistry - A European Journal **2006**, 12 (17), 4478-4494.
(22) Angelomé, P. C.; Fuertes, M. C., Metal Nanoparticles-Mesoporous Oxide Nanocomposite Thin Films. In Handbook of Sol-Gel Science and Technology, Klein, L.; Aparicio, M.; Jitianu, A., Eds. Springer International Publishing: Cham, **2018**; pp 2507-2533
(23) Innocenzi, P.; Malfatti, L., Nanoparticles in mesoporous films, a happy marriage for materials science. J. Nanopart. Res. **2018**, 20 (6), 167.
(24) Lionello, D. F.; Steinberg, P. Y.; Zalduendo, M. M.; Soler-Illia, G. J. A. A.; Angelomé, P. C.; Fuertes, M. C., Structural and Mechanical Evolution of Mesoporous Films with Thermal Treatment: The Case of Brij 58 Templated Titania. The Journal of Physical Chemistry C **2017**, 121 (40), 22576-22586.
(25) Angelomé, P. C.; Andrini, L.; Calvo, M. E.; Requejo, F. G.; Bilmes, S. A.; Soler-Illia, G. J. A. A., Mesoporous Anatase TiO2 Films: Use of Ti K XANES for the Quantification of the Nanocrystalline Character and Substrate Effects in the Photocatalysis Behavior. The Journal of Physical Chemistry C **2007**, 111 (29), 10886-10893.
(26) Violi, I. L.; Perez, M. D.; Fuertes, M. C.; Soler-Illia, G. J. d. A. A., Highly ordered, accessible and nanocrystalline mesoporous TiO2 thin films on transparent conductive substrates. ACS Applied Materials Interfaces **2012**, 4 (8), 4320-30.
(27) Fuertes, M. C.; Marchena, M.; Marchi, M. C.; Wolosiuk, A.; Soler-Illia, G. J. A. A., Controlled Deposition of Silver Nanoparticles in Mesoporous Single- or Multilayer Thin Films: From Tuned Pore Filling to Selective Spatial Location of Nanometric Objects. Small **2009**, 5 (2), 272-280.
(28) Boissière, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C., Porosity and Mechanical Properties of Mesoporous Thin Films Assessed by Environmental Ellipsometric Porosimetry. Langmuir **2005**, 21 (26), 12362-12371.
(29) Das, S.; Wu, Q.; Garlapalli, R. K.; Nagpure, S.; Strzalka, J.; Jiang, Z.; Rankin, S. E., In-Situ GISAXS Investigation of Pore Orientation Effects on the Thermal Transformation Mechanism in Mesoporous Titania Thin Films. The Journal of Physical Chemistry C **2014**, 118 (2), 968-976.
(30) Gonzalez Solveyra, E.; Fuertes, M. C.; Soler-Illia, G. J. A. A.; Angelomé, P. C., 2D-SAXS In Situ Measurements as a Tool To Study Elusive Mesoporous Phases: The Case of p6mm TiO2. J. Phys. Chem. C **2017**, 121 (6), 3623-3631.
(31) Innocenzi, P.; Kidchob, T.; Malfatti, L.; Costacurta, S.; Takahashi, M.; Piccinini, M.; Marcelli, A., In-situ study of sol–gel processing by time-resolved infrared spectroscopy. Journal of Sol-Gel Science and Technology **2008**, 48 (1-2), 253-259.
(32) Koganti, V. R.; Das, S.; Rankin, S. E., In Situ FTIR Investigation of the Kinetics of Silica Polycondensation in Surfactant Templated, Mesostructured Thin Films. The Journal of Physical Chemistry C **2014**, 118 (33), 19450-19461.
(33) Grosso, D.; Cagnol, F.; Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Amenitsch, H.; Brunet-Bruneau, A.; Bourgeois, A.; Sanchez, C., Fundamentals of Mesostructuring Through Evaporation-Induced Self-Assembly. Advanced Functional Materials **2004**, 14, 309.
(34) Crepaldi, E. L.; Soler-Illia, G. J. d. A. A.; Bouchara, A.; Grosso, D.; Durand, D.; Sanchez, C., Controlled Formation of Highly Ordered Cubic and Hexagonal Mesoporous Nanocrystalline Yttria–Zirconia and Ceria–Zirconia Thin Films Exhibiting High Thermal Stability. Angewandte Chemie International Edition **2003**, 42 (3), 347-351.
(35) Zelcer, A.; Soler-Illia, G. J. A. A., One-step preparation of UV transparent highly ordered mesoporous zirconia thin films. Journal of Materials Chemistry C **2013**, 1 (7), 1359-1367.
(36) Malfatti, L.; Kidchob, T.; Costacurta, S.; Falcaro, P.; Schiavuta, P.; Amenitsch, H.; Innocenzi, P., Highly Ordered Self-Assembled Mesostructured Hafnia Thin Films: An Example of Rewritable Mesostructure. Chemistry of Materials **2006**, 18 (19), 4553-4560.
(37) Nicole, L.; Boissiere, C.; Grosso, D.; Hesemann, P.; Moreau, J.; Sanchez, C., Advanced selective optical sensors based on periodically organized mesoporous hybrid silica thin films. Chem. Comm. **2004**, (20), 2312-2313.
(38) Wirnsberger, G.; Scott, B. J.; Stucky, G. D., pH Sensing with mesoporous thin films. Chem. Comm. **2001**, (1), 119-120.

(39) Melde, B.; Johnson, B.; Charles, P., Mesoporous Silicate Materials in Sensing. Sensors **2008**, 8 (8), 5202-5228.
(40) Bearzotti, A.; Bertolo, J. M.; Innocenzi, P.; Falcaro, P.; Traversa, E., Humidity sensors based on mesoporous silica thin films synthesised by block copolymers. J. Eur. Ceram. Soc. **2004**, 24 (6), 1969-1972.
(41) Bearzotti, A.; Mio Bertolo, J.; Innocenzi, P.; Falcaro, P.; Traversa, E., Relative humidity and alcohol sensors based on mesoporous silica thin films synthesised from block copolymers. Sensors and Actuators, B: Chemical **2003**, 95 (1-3), 107-110.
(42) Falcaro, P.; Bertolo, J. M.; Innocenzi, P.; Amenitsch, H.; Bearzotti, A., Ordered mesostructured silica films: Effect of pore surface on its sensing properties. J. Sol-Gel Sci. Technol. **2004**, 32 (1-3), 107-110.
(43) Innocenzi, P.; Falcaro, P.; Bertolo, J. M.; Bearzotti, A.; Amenitsch, H., Electrical responses of silica mesostructured films to changes in environmental humidity and processing conditions. J. Non-Cryst. Solids **2005**, 351 (24-26), 1980-1986.
(44) Lee, H. J.; Park, K. K.; Kupnik, M.; Melosh, N. A.; Khuri-Yakub, B. T., Mesoporous thin-film on highly-sensitive resonant chemical sensor for relative humidity and CO2 detection. Anal. Chem. **2012**, 84 (7), 3063-3066.
(45) Innocenzi, P.; Martucci, A.; Guglielmi, M.; Bearzotti, A.; Traversa, E.; Pivin, J. C., Mesoporous silica thin films for alcohol sensors. J. Eur. Ceram. Soc. **2001**, 21 (10-11), 1985-1988.
(46) Tu, J.; Li, N.; Geng, W.; Wang, R.; Lai, X.; Cao, Y.; Zhang, T.; Li, X.; Qiu, S., Study on a type of mesoporous silica humidity sensing material. Sensors and Actuators B: Chemical **2012**, 166-167 (0), 658-664.
(47) Domansky, K.; Liu, J.; Wang, L. Q.; Engelhard, M. H.; Baskaran, S., Chemical sensors based on dielectric response of functionalized mesoporous silica films. J. Mater. Res. **2001**, 16 (10), 2810-2816.
(48) Schlücker, S., Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications. Angewandte Chemie International Edition **2014**, 53 (19), 4756-4795.
(49) Xie, W.; Schlücker, S., Medical applications of surface-enhanced Raman scattering. Phys. Chem. Chem. Phys. **2013**, 15 (15), 5329-5344.
(50) Alvarez-Puebla, R. A.; Liz-Marzán, L. M., SERS Detection of Small Inorganic Molecules and Ions. Angewandte Chemie International Edition 2012, 51 (45), 11214-11223.
(51) Kneipp, K., Surface-enhanced Raman scattering. Phys. Today **2007**, 60 (11), 40-46.
(52) Steinberg, P. Y.; Zalduendo, M. M.; Giménez, G.; Soler-Illia, G. J. d. A. A.; Angelomé, P. C., TiO2 mesoporous thin films architecture as a tool to control Au nanoparticles growth and sensing capabilities. Phys. Chem. Chem. Phys. **2019**.
(53) López-Puente, V.; Abalde-Cela, S.; Angelomé, P. C.; Alvarez-Puebla, R. A.; Liz-Marzán, L. M., Plasmonic Mesoporous Composites as Molecular Sieves for SERS Detection. The Journal of Physical Chemistry Letters **2013**, 4 (16), 2715-2720.
(54) Wolosiuk, A.; Tognalli, N. G.; Martínez, E. D.; Granada, M.; Fuertes, M. C.; Troiani, H.; Bilmes, S. A.; Fainstein, A.; Soler-Illia, G. J. A. A., Silver Nanoparticle-Mesoporous Oxide Nanocomposite Thin Films: A Platform for Spatially Homogeneous SERS-Active Substrates with Enhanced Stability. ACS Appl. Mater. Interfaces **2014**, 6 (7), 5263-5272.
(55) López-Puente, V.; Angelomé, P. C.; Soler-Illia, G. J. A. A.; Liz-Marzán, L. M., Selective SERS Sensing Modulated by Functionalized Mesoporous Films. ACS Appl. Mater. Interfaces **2015**, 7 (46), 25633-25640.
(56) Zalduendo, M. M.; Langer, J.; Giner-Casares, J. J.; Halac, E. B.; Soler-Illia, G. J. A. A.; Liz-Marzán, L. M.; Angelomé, P. C., Au Nanoparticles–Mesoporous TiO2 Thin Films Composites as SERS Sensors: A Systematic Performance Analysis. The Journal of Physical Chemistry C **2018**, 122 (24), 13095-13105.
(57) Wang, Y.-W.; Kao, K.-C.; Wang, J.-K.; Mou, C.-Y., Large-Scale Uniform Two-Dimensional Hexagonal Arrays of Gold Nanoparticles Templated from Mesoporous Silica Film for Surface-Enhanced Raman Spectroscopy. The Journal of Physical Chemistry C **2016**, 120 (42), 24382-24388.
(58) Malfatti, L.; Falcaro, P.; Marmiroli, B.; Amenitsch, H.; Piccinini, M.; Falqui, A.; Innocenzi, P., Nanocomposite mesoporous ordered films for lab-on-chip intrinsic surface enhanced Raman scattering detection. Nanoscale **2011**, 3 (9), 3760-6.
(59) Angelomé, P. C.; Liz-Marzán, L. M., Monitoring Solvent Evaporation from Thin Films by Localized Surface Plasmon Resonance Shifts. J. Phys. Chem. C **2010**, 114 (43), 18379-18383.
(60) Angelomé, P. C.; Pastoriza-Santos, I.; Pérez Juste, J.; Rodríguez-González, B.; Zelcer, A.; Soler-Illia, G. J. A. A.; Liz Marzán, L. M., Growth and Branching of Gold Nanoparticles Through Mesoporous Silica Thin Films. Nanoscale **2012**, 4, 931-939.
(61) Sánchez, V. M.; Martínez, E. D.; Martínez Ricci, M. L.; Troiani, H.; Soler-Illia, G. J. A. A., Optical Properties of Au Nanoparticles Included in Mesoporous TiO2 Thin Films: A Dual Experimental and Modeling Study. The Journal of Physical Chemistry C **2013**, 117 (14), 7246-7259.
(62) Wei, H.; Xu, H., Hot spots in different metal nanostructures for plasmon-enhanced Raman spectroscopy. Nanoscale **2013**, 5 (22), 10794-10805.
(63) Reguera, J.; Langer, J.; Jimenez de Aberasturi, D.; Liz-Marzan, L. M., Anisotropic metal nanoparticles for surface enhanced Raman scattering. Chem. Soc. Rev. **2017**, 46 (13), 3866-3885.
(64) Bodelon, G.; Montes-Garcia, V.; Lopez-Puente, V.; Hill, E. H.; Hamon, C.; Sanz-Ortiz, M. N.; Rodal-Cedeira, S.; Costas, C.; Celiksoy, S.; Perez-Juste, I.; Scarabelli, L.; La Porta, A.; Perez-Juste, J.; Pastoriza-Santos, I.;

Liz-Marzan, L. M., Detection and imaging of quorum sensing in Pseudomonas aeruginosa biofilm communities by surface-enhanced resonance Raman scattering. Nat. Mater. 2016, 15 (11), 1203-1211.
(65) Joannopoulos, J. D.; Johnson, S. G.; Winn, J. N.; Meade, R. D., Photonic crystals: Molding the flow of light. **2011**.
(66) Burgess, I. B.; Lončar, M.; Aizenberg, J., Structural colour in colourimetric sensors and indicators. Journal of Materials Chemistry C **2013**, 1 (38), 6075-6086.
(67) Fenzl, C.; Hirsch, T.; Wolfbeis, O. S., Photonic Crystals for Chemical Sensing and Biosensing. Angew. Chem. Int. Ed. **2014**, 53 (13), 3318-3335.
(68) Inan, H.; Poyraz, M.; Inci, F.; Lifson, M. A.; Baday, M.; Cunningham, B. T.; Demirci, U., Photonic crystals: Emerging biosensors and their promise for point-of-care applications. Chemical Society Reviews **2017**, 46 (2), 366-388.
(69) Shen, H.; Wang, Z.; Wu, Y.; Yang, B., One-dimensional photonic crystals: Fabrication, responsiveness and emerging applications in 3D construction. RSC Advances **2016**, 6 (6), 4505-4520.
(70) Xu, H.; Wu, P.; Zhu, C.; Elbaz, A.; Gu, Z. Z., Photonic crystal for gas sensing. Journal of Materials Chemistry C **2013**, 1 (38), 6087-6098.
(71) Huang, S. G.; Chen, K. P.; Jeng, S. C., Phase sensitive sensor on Tamm plasmon devices. Optical Materials Express **2017**, 7 (4).
(72) Kaliteevski, M.; Iorsh, I.; Brand, S.; Abram, R. A.; Chamberlain, J. M.; Kavokin, A. V.; Shelykh, I. A., Tamm plasmon-polaritons: Possible electromagnetic states at the interface of a metal and a dielectric Bragg mirror. Physical Review B **2007**, 76 (16), 165415.
(73) Paulauskas, A.; Tumenas, S.; Selskis, A.; Tolenis, T.; Valavicius, A.; Balevicius, Z., Hybrid Tamm-surface plasmon polaritons mode for detection of mercury adsorption on 1D photonic crystal/gold nanostructures by total internal reflection ellipsometry. Optics Express **2018**, 26 (23), 30400-30408.
(74) Sasin, M. E.; Seisyan, R. P.; Kaliteevski, M. A.; Brand, S.; Abram, R. A.; Chamberlain, J. M.; Iorsh, I. V.; Shelykh, I. A.; Egorov, A. Y.; Vasil'ev, A. P.; Mikhrin, V. S.; Kavokin, A. V., Tamm plasmon-polaritons: First experimental observation. Superlattices and Microstructures **2010**, 47 (1), 44-49.
(75) Auguié, B.; Fuertes, M. C.; Angelomé, P. C.; López Abdala, N.; Soler Illia, G. J. A. A.; Fainstein, A., Tamm Plasmon Resonance in Mesoporous Multilayers: Toward a Sensing Application. ACS Photonics **2014**, 1 (9), 775-780.
(76) Colodrero, S.; Ocaña, M.; González-Elipe, A. R.; Míguez, H., Response of Nanoparticle-Based One-Dimensional Photonic Crystals to Ambient Vapor Pressure. Langmuir **2008**, 24 (16), 9135-9139.
(77) Colodrero, S.; Ocaña, M.; Míguez, H., Nanoparticle-Based One-Dimensional Photonic Crystals. Langmuir **2008**, 24 (9), 4430-4434.
(78) Kobler, J.; Lotsch, B. V.; Ozin, G. A.; Bein, T., Vapor-Sensitive Bragg Mirrors and Optical Isotherms from Mesoporous Nanoparticle Suspensions. ACS Nano **2009**, 3 (7), 1669-1676.
(79) Puzzo, D. P.; Bonifacio, L. D.; Oreopoulos, J.; Yip, C. M.; Manners, I.; Ozin, G. A., Color from colorless nanomaterials: Bragg reflectors made of nanoparticles. Journal of Materials Chemistry **2009**, 19 (21), 3500.
(80) Wang, L.; Zhang, S.; Lutkenhaus, J. L.; Chu, L.; Tang, B.; Li, S.; Ma, W., All nanoparticle-based P(MMA–AA)/TiO2 one-dimensional photonic crystal films with tunable structural colors. Journal of Materials Chemistry C **2017**, 5 (32), 8266-8272.
(81) Fuertes, M. C.; Colodrero, S.; Lozano, G.; González-Elipe, A. R.; Grosso, D.; Boissière, C.; Sánchez, C.; Soler-Illia, G. J. d. A. A.; Míguez, H., Sorption Properties of Mesoporous Multilayer Thin Films. The Journal of Physical Chemistry C **2008**, 112 (9), 3157-3163.
(82) Fuertes, M. C.; López-Alcaraz, F. J.; Marchi, M. C.; Troiani, H. E.; Luca, V.; Míguez, H.; Soler-Illia, G. J. A. A., Photonic Crystals from Ordered Mesoporous Thin-Film Functional Building Blocks. Advanced Functional Materials **2007**, 17 (8), 1247-1254.
(83) Ghazzal, M. N.; Deparis, O.; Errachid, A.; Kebaili, H.; Simonis, P.; Eloy, P.; Vigneron, J. P.; De Coninck, J.; Gaigneaux, E. M., Porosity control and surface sensitivity of titania/silica mesoporous multilayer coatings: applications to optical Bragg resonance tuning and molecular sensing. Journal of Materials Chemistry **2012**, 22 (48), 25302-25310.
(84) Ghazzal, M. N.; Deparis, O.; De Coninck, J.; Gaigneaux, E. M., Tailored refractive index of inorganic mesoporous mixed-oxide Bragg stacks with bio-inspired hygrochromic optical properties. Journal of Materials Chemistry C **2013**, 1 (39), 6202-6209.
(85) Ghazzal, M. N.; Joseph, M.; Kebaili, H.; De Coninck, J.; Gaigneaux, E. M., Tuning the selectivity and sensitivity of mesoporous dielectric multilayers by modifiying the hydrophobic–hydrophilic balance of the silica layer. Journal of Materials Chemistry **2012**, 22 (42), 22526-22532.
(86) Martínez Gazoni, R.; Bellino, M. G.; Cecilia Fuertes, M.; Giménez, G.; Soler-Illia, G. J. A. A.; Ricci, M. L. M., Designed nanoparticle–mesoporous multilayer nanocomposites as tunable plasmonic–photonic architectures for electromagnetic field enhancement. Journal of Materials Chemistry C **2017**, 5 (14), 3445-3455.
(87) Choi, S. Y.; Mamak, M.; von Freymann, G.; Chopra, N.; Ozin, G. A., Mesoporous Bragg Stack Color Tunable Sensors. Nano Lett. **2006**, 6 (11), 2456-2461.
(88) Hidalgo, N.; Calvo, M. E.; Bellino, M. G.; Soler-Illia, G. J. A. A.; Míguez, H., Porous supramolecularly

templated optical resonators built in 1D photonic crystals. Advanced Functional Materials **2011**, 21 (13), 2534-2540.
(89) Hidalgo, N.; Calvo, M. E.; Míguez, H., Mesostructured Thin Films as Responsive Optical Coatings of Photonic Crystals. Small **2009**, 5 (20), 2309-2315.
(90) Sansierra, M. C.; Morrone, J.; Cornacchiulo, F.; Fuertes, M. C.; Angelomé, P. C., Detection of Organic Vapors Using Tamm Mode Based Devices Built from Mesoporous Oxide Thin Films. ChemNanoMat **2019**, 5 (10), 1289-1295.
(91) Bonifacio, L. D.; Ozin, G. A.; Arsenault, A. C., Photonic Nose–Sensor Platform for Water and Food Quality Control. Small **2011**, 7 (22), 3153-3157.
(92) Bonifacio, L. D.; Puzzo, D. P.; Breslav, S.; Willey, B. M.; McGeer, A.; Ozin, G. A., Towards the Photonic Nose: A Novel Platform for Molecule and Bacteria Identification. Advanced Materials **2010**, 22 (12), 1351-1354.

M. Mercedes Zalduendo obtained her degree in Chemistry from Universidad de Buenos Aires in 2014. She joined the Chemistry of Nanomaterials Group and started her PhD in Chemistry in 2015, financed by CONICET, under the supervision of Dr. Paula C. Angelomé. Her thesis is focused on the study of Mesoporous Nanocomposite Thin Films and their applications as optical platforms. She worked for some months in the Bionanoplasmonics Lab (CIC-Biomagune, San Sebastián, Spain) where she studied the SERS sensing capabilities of different platforms.

Josefina Morrone obtained her degree in Chemical Sciences in 2016 at the Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires. In 2017, she started her PhD financed by CONICET at Universidad Nacional de San Martín, under the guide of Dr. María Cecilia Fuertes and Dr. Paula C. Angelomé. Her thesis is focused on the design, construction and characterization of structural and optical properties of sensors based on photonic crystals from ordered mesoporous oxides. During 2018, Josefina stayed for 3 month in the Hybrid materials and Nano-materials Team, in the Sorbonne Université located in Paris (France), under the supervision of Dr. Cédric Boissiere, where she trained about different characterization techniques using ellipsometry.

Paula Y. Steinberg got her degree in chemistry in 2010 and her PhD in chemistry in 2018, both at the Universidad de Buenos Aires, Argentina. Her PhD was developed at the Chemistry of Nanomaterials group (Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Argentina) and financed by CONICET. Dr. Paula C. Angelomé and Dr. Galo J. A. A. Soler-Illia were her advisors. Her PhD thesis concerned the study of the structural control of TiO_2 mesoporous thin films and its effects on the transport and reactivity within confined environments. During 2016, Paula participated in an Elettra synchrotron campaign to study de use of deep X-ray as a novel method to synthesize mesoporous oxides thin films.

M. Cecilia Fuertes obtained a Materials Engineer Degree in 2003, from de University of Mar del Plata, a Master in Material Science (2005) and a PhD in Materials Science and Technology (2009), both from the Sabato Institute-CNEA and the University of San Martín. Her thesis, under direction of Prof. Soler-Illia, was focused on the synthesis and characterization of multiscale materials based on mesoporous oxide thin films. She worked as a postdoctoral fellow at the Solar Energy Division (CNEA), with Dr. Plá (2009-11). From 2011, she is a CONICET staff scientist at CNEA, Buenos Aires, Argentina. Her current main interests include the design, production and characterization of functional nanomaterials and thin films, with applications in optical devices and sensors. She has published 28 scientific papers and a book chapter, has been in charge of national research projects and has supervised PhD, MSc and degree students.

Paula C. Angelomé obtained a Chemistry Degree (2003) and PhD (2008) from University of Buenos Aires (Argentina). During her doctoral thesis, performed under the supervision of Dr. Galo Soler-Illia at CAC-CNEA, she worked on synthesis and characterization of mesoporous metallic, mixed and hybrid oxide thin films. Between 2008 and 2012 she was a postdoctoral fellow in the Colloid Chemistry Group (University of Vigo, Spain) under the direction of Prof. Luiz Liz-Marzán, working on synthesis and applications of metallic nanoparticles and composites. She came back to CNEA in 2012, as a CONICET Researcher and, since 2017, she holds an Independent Research position. She has published more than 35 scientific papers, has been in charge of several national and international research projects and has supervised several postdocs and PhD, MSc and degree students.