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Synthesis and applications of mesoporous nanocomposites containing metal nanoparticles

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Abstract Metal nanoparticles (NP) and mesoporous (MP) oxides are complementary materials, since the size scale of pores in MP oxides matches that of NP and both systems have potential applications in similar fields. Besides, nanocomposites obtained through their combination possess not only the intrinsic properties of each component, but also new features derived from the synergy between them, mainly due to the high interfacial area between the metal and the oxide. Thus, new optical, catalytic and sensing properties can be achieved that are not easily available from the individual components. In this review, we focus our attention on such NP@MP composites, not only from the point of view of the most common synthesis pathways but also briefly describing their applications in fields as diverse as (photo)catalysis, sensing, photochromism and other optical properties, as well as patterning.

Keywords Metal nanoparticles · Mesoporous oxides · Thin films · Sensors · Catalysis

1 Introduction

The renewed interest that metal nanoparticles (NP) have raised during the past decade has been motivated by their various special properties, which give rise to potential applications in diverse fields [1, 2], with a particularly strong focus on their catalytic and optical properties. The use of NP in catalysis is related in part to their high specific surface area but also to their high surface reactivity, which may drastically change as compared with their bigger counterparts [3, 4]. The field of NP catalysis is often termed “semi-heterogeneous catalysis”, as it is at the frontier between homogeneous and heterogeneous catalysis. NP catalysis has been applied for a large amount of organic reactions, but mainly in redox catalysis, photocatalysis (photocatalytic water splitting and photo-hydrogenation of alkenes, alkynes, and CO₂), hydrogenation and oxidation [4]. On the other hand, the optical properties of NP are related to localized surface plasmon resonances (LSPR) [5, 6], which give rise to intense extinction bands in the visible and NIR, as well as high electric field enhancements at the NP surface [7]. The optical response of NP can be tuned by modifying their size and shape, as well as their dielectric environment (refractive index of the surrounding medium, presence of neighboring particles, etc.) [8]. These interesting optical properties make metal NP interesting for use in diverse fields such as (bio)sensors [9], surface enhanced Raman scattering (SERS) [10], production of devices that require light confinement (solar cells, vapor production, local heating, etc.) [11, 12] and biological applications (disease diagnosis and phototherapy, drug delivery, etc.) [12, 13].

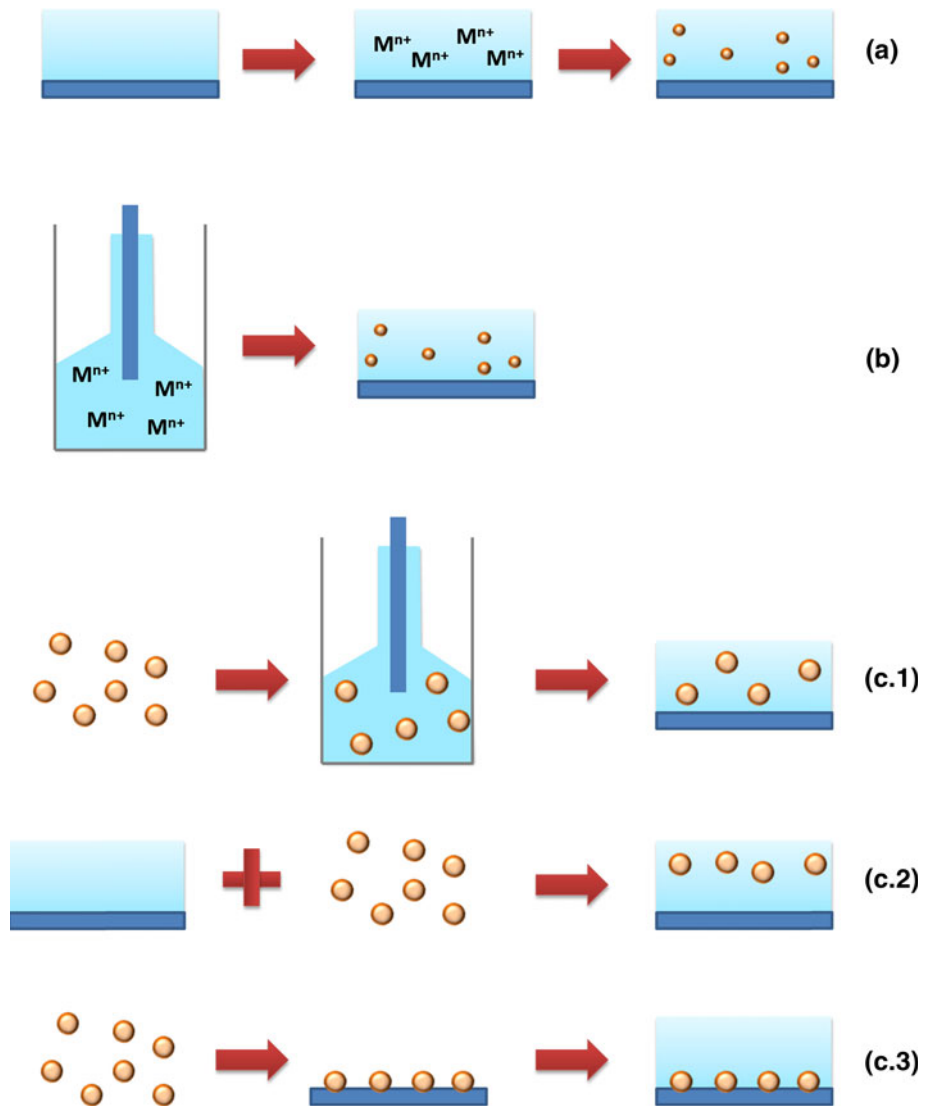
P. C. Angelomé (✉)
Gerencia Química, Centro Atómico Constituyentes, Comisión
Nacional de Energía Atómica, Av. General Paz 1499,
B1650KNA San Martín, Buenos Aires, Argentina
e-mail: angelome@cnea.gov.ar

L. M. Liz-Marzán (✉)
Bionanoplasmonics Laboratory, CIC biomaGUNE, Paseo de
Miramón 182, 20009 Donostia-San Sebastián, Spain
e-mail: llizmarzan@cicbiomagune.es

L. M. Liz-Marzán
Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain

L. M. Liz-Marzán
Departamento de Química Física, Universidade de Vigo,
36310 Vigo, Spain

Fig. 1 Scheme of the different alternatives to prepare NP@MP composite films: **a** Impregnation and reduction, **b** one-pot method and **c** use of pre-synthesized particles

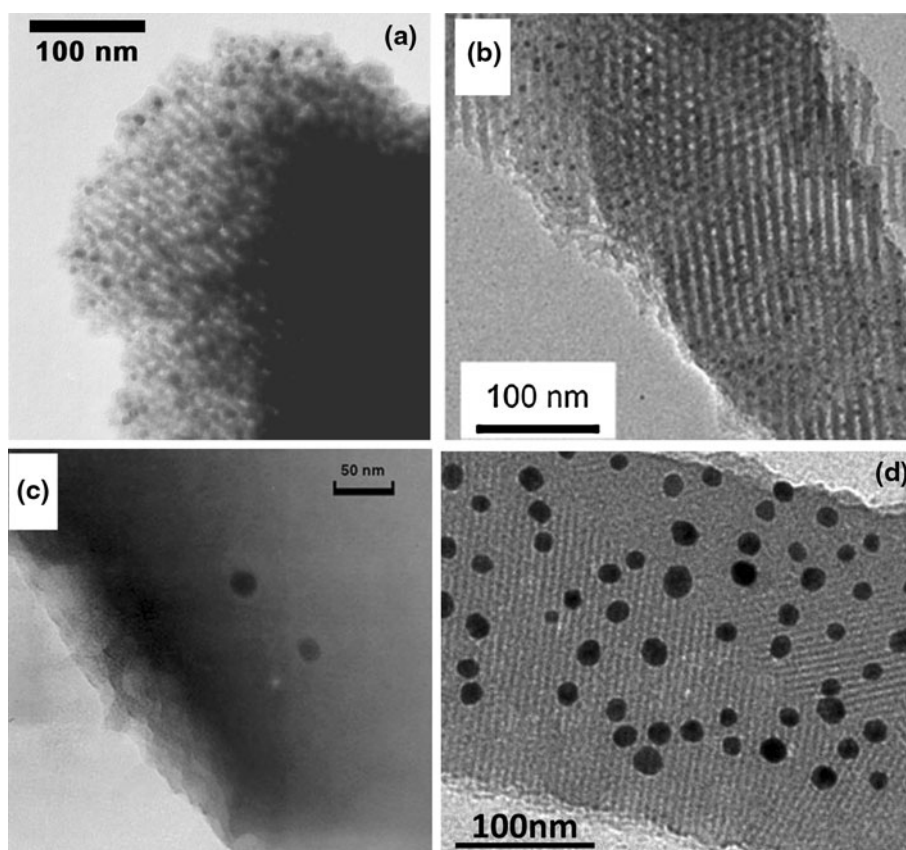


Due to the close relationship between synthesis, properties and applications, the synthesis of NP has been extensively developed during the last decades [1] and a wide variety of morphologies can be obtained in a reproducible way by means of colloid chemistry methods. Readily obtainable morphologies include spheres, nanorods, various polyhedra, nanostars and nanoplates [1, 14]. On the other hand, the synthesis of mesoporous (MP, pore diameters between 2 and 50 nm) oxides has also experienced an important development during the last 20 years. These materials are prepared combining the self-assembly of amphiphilic molecules (which act as templates) and sol-gel reactions (which give rise to the oxide), thereby leading to materials with extremely high specific surface area and highly ordered arrays of monodisperse pores. The field started its development with the MCM silica family [15], but an increasing amount of mesoporous materials with diverse chemical compositions, shaped as powders,

monoliths, thin films, membranes, or fibers have also been developed [16–18]. MP oxide thin films (especially SiO_2 and TiO_2) are particularly interesting [19] because they can be easily extracted from a medium, thus rendering them ideal for applications that require reusability. Additionally, they show a high ability for integration in current material processing technologies, due to the high flexibility of its synthesis.

Metal NP and MP oxides can somehow complement each other, since the pores are complementary with the particles, both in size and potential applications. The obtained NP@MP composites possess the intrinsic properties of each family, but also new features derived from the synergy between the components, mainly due to the large interfacial area between the metal and the oxide. Powder NP@MP composites have been recently investigated in great detail, and several excellent reviews have been published on this subject [20, 21]. In this review, we

Fig. 2 TEM images of different NP@MP composite films: **a** Ag NP@MP TiO₂ obtained by impregnation and reduction (reproduced with permission from Ref. [38]. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim); **b** Ag NP@MP SiO₂ obtained by one-pot synthesis (Reproduced from Ref. [47] with permission from The Royal Society of Chemistry); **c** Au NP@MP SiO₂ obtained using NP suspended in the sol (reproduced with permission from Ref. [48] Copyright © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); **d** Au NP@MP SiO₂ obtained by adhesion of NP to a substrate followed by film deposition



focus our attention towards NP@MP composites prepared by combining MP oxide thin films and metal NP. We describe the most common synthesis methods as well as tested and potential applications.

2 Synthesis methods

Three general synthesis methods are commonly used for the preparation of NP@MP composite films. These methods are summarized in Fig. 1, and explained in this section.

2.1 Impregnation and reduction

The impregnation and reduction approach is, by far, the most common method for the preparation of NP@MP composite films. The general idea behind this process is depicted in Fig. 1a. In a first step, the MP films are prepared, usually by *Evaporation Induced Self-Assembly* [22], and the template is then eliminated by either thermal treatment or solvent extraction. Once the pores are emptied, the metal salt is adsorbed, which may involve electrostatic forces (for Ag(I) adsorption [23–30]), or specific interactions with amino groups (for Au(III)) [31–33], but trapping within polyelectrolyte brushes [34] has also been tested. In all cases, reduction of the metal ions into metallic

particles is the last step. The reduction can be performed by thermal treatment [23], UV irradiation [27, 35–37] or by chemical reduction, using formaldehyde [38, 39], hydrogen gas [25, 29, 31, 32, 36, 40–42] or NaBH₄ [30, 34, 39], among other reducing agents. It has been demonstrated that the NP size and spatial distribution within the film depends on the specific reducing treatment [28], particularly on the strength of the selected reducing agent. It should be noted that most often a single impregnation and reduction cycle is not sufficient to fill the pores completely, since the number of metal ions that can be adsorbed is limited. Nevertheless, the impregnation–reduction cycle can be repeated several times, which allows to control the amount of metal formed inside the pores. Interestingly, the final particle shape is determined by the pore size and connectivity. Thus, spherical NP are obtained in most cases, as can be seen in Fig. 2a. The main drawbacks of this approach are the lack of control in the location of the NP within the film and the formation of an unwanted metallic layer on top of the films [37, 39], but both problems can be overcome by modifying the synthesis procedure.

A variation of this method is the electrochemically induced impregnation and reduction [24, 43–45]. In this case, the film is supported onto a conductive substrate, which is used as a working electrode. Subsequently, immersion in an Au(III) or Pt(IV) solution and application

of an electrical potential leads to metal deposition. The metal may completely replicate the pore array, and it is even possible to dissolve the oxide leaving a metallic mesoporous material [44, 45]. Another variation of the method was proposed by Bois and coworkers [46], comprising the impregnation of Ag(I) in a mesostructured film (i.e., with the template still inside the pores). In this case, the metal is formed only on the topmost pore layer, which facilitates the control over the final particle shape by controlling the pore array, which is an interesting approach e.g. to obtain rod shaped NP. Further work to reproduce and expand these findings with MP films would be really interesting.

2.2 One pot synthesis

In this approach, a metal salt is included in the sol mixture that gives rise to the MP films, as shown in Fig. 1b. As the sols are highly acidic, the metal salt is stable under those conditions and the film deposition can be performed as usual. Both the oxide and the particles are formed at the same time under laser irradiation [49], X-ray irradiation [47, 50] or conventional thermal treatment [51–53]. Using this methodology, the obtained particles are small (due to the limited amount of metal salt that can be loaded in the sol) and are distributed both inside the oxide framework and at the surface of the pores. An example of a typical NP distribution is presented in Fig. 2b, where the small dark dots are Ag NP. In principle, due to their different localization, these NP are expected to be less accessible for chemical reactions, as compared to those obtained by the impregnation–reduction method, since a portion of the total metallic surface is covered by the oxide. However, no studies about this subject have been presented so far, rendering this topic an open question that should be studied in the future. Nevertheless, the method does provide a simple way to obtain metallic patterns inside the MP framework, as discussed in the applications section below.

2.3 Use of preformed particles

In all its variations, this method requires the preparation of metal NP by a colloid chemistry method before their incorporation within the film. Thus, both the size and shape of the NP can be defined prior to MP oxide synthesis and it is not restricted to spherical particles. However, these methods do not allow a high NP loading, as a consequence of the low NP concentrations in usual metal colloids.

2.3.1 Incorporation of particles within the sol

This method (schematically depicted in Fig. 1c.1) is rare, since metallic NP are usually unstable under the conditions

required to prepare a stable sol (highly concentrated acidic medium, organic solvents). Consequently, this method requires a careful selection of the NP stabilizer, so as to make them compatible with the properties of the sols. Additionally, the NP size and shape should be controlled to allow formation of a smooth film, without cracks or thickness variations. An example of this method is the work by Goettmann et al. [48], who used Au NP stabilized by a phosphinine ligand to prepare composites with SiO₂ MP films (Fig. 2c). The NP were introduced in the silica sol just before deposition in a mass ratio (calculated on the basis of the final SiO₂ mass) of 0.5, 2, 5, and 10 % but only the samples with NP content below 2 % showed good optical quality. This work was later extended by the same group to Pd NP and MP TiO₂ films [54]. Another approach was tested by Yang et al. [55], who included Au rods@-SiO₂ in a sol with silica precursors and obtained a composite in which the rods are first surrounded by a dense silica shell and then embedded in a MP film, which had been previously used for incorporation in standard silica gels [56, 57]. In this case however, access to the particles is severely restricted, since they are surrounded by a microporous silica shell.

2.3.2 Particle diffusion thorough the film

This method (depicted in Fig. 1c.2) is also unusual, since it requires the use of particles that are small enough to diffuse between the pores and the connecting necks [58, 59]. To improve diffusion, Patel et al. [60] used electrophoretic deposition to include 3.1 nm Au nanocrystals stabilized by dodecanethiol within TiO₂ MP thin films (deposited onto a conductive substrate). With this methodology, Au nanocrystal loadings up to 21 wt% were reached. However, in all cases an irregular distribution along the film thickness was obtained, since the tortuosity of the MP films does not allow the diffusion of the particles to the innermost layer of pores.

2.3.3 Adhesion of particles to a substrate followed by film deposition

This method has been recently reported by our group [61–63] and represents a new approach that is schematically shown in Fig. 1c.3: a sub-monolayer of NP (spheres with different diameters, decahedra or other shapes) are chemically bound to a glass slide and subsequently covered with a MP thin film. The method allows obtaining fully covered metallic NP and well-ordered MP thin films. With this approach, the particles (whose shape and size can be finely tuned by well-known colloid chemistry methods) underneath the porous films remain accessible but not in direct contact with the medium, opening the way toward new

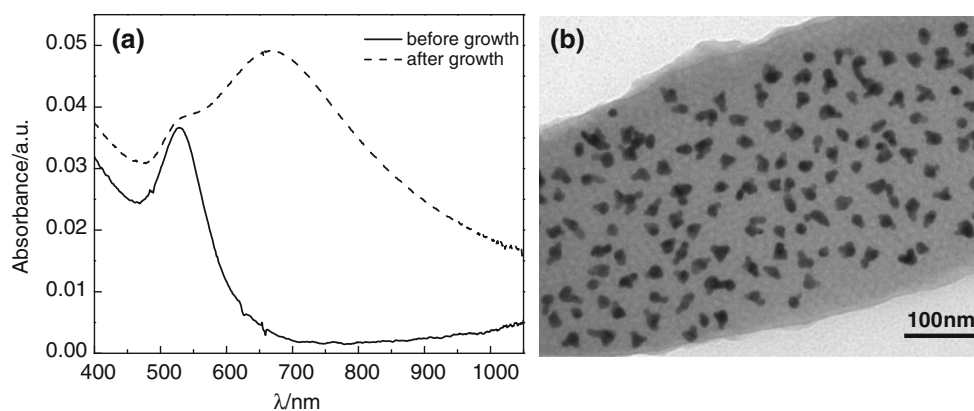


Fig. 3 **a** UV-vis spectra before and after seeded growth of 15 nm Au spheres covered by SiO₂ MP film (template with block copolymer Pluronic F127); **b** TEM image of the composite after growth, showing “hairy” NP

applications. An example of this type of composites is presented in Fig. 2d. In a second step, the NP shape can be modified by seeded growth [62, 63], which allows obtaining either larger NP or even “hairy” NP (Fig. 3b), depending on the mesoporous material used and the growth conditions. By this procedure, it was possible to obtain novel NP shapes that are neither easily obtained in solution nor easily encapsulated within oxide films. Interestingly, such templated growth leads to intense and useful optical changes in the nanocomposite material (Fig. 3a).

3 Applications

Although the literature has so far mainly focused on synthetic methods to obtain NP@MP composites, several examples have also been presented on the possible applications of these materials. We review in the following subsections some of the most usual and (in our view) interesting applications.

3.1 Catalysis

In traditional catalysis of organic reactions by metals, inclusion of the NP inside MP films allows easy recovery and recycling of the catalyst [59] and may also influence the activity and selectivity of the reactions [64]. For example, Cortial et al. [54] tested Au NP@TiO₂ as catalyst for glycol oxidation and Pd NP@SiO₂ to catalyze the allylic amination of cinnamyl acetate by benzylamine. In the latter case, they found that immobilized NP were three orders of magnitude more active than their homogeneous counterparts and that the regioselectivity was totally in favor of one of the possible products. In the case of photocatalysis by semiconductors (SC), a synergic effect occurs: it has been demonstrated that metal NP can

improve the electron flow from the SC surface to the metal, thereby suppressing electron-hole recombination, one of the main causes of activity loss of the photocatalysts. Thus, several groups tried to improve the photocatalytic activity of MP TiO₂ by including Au or Ag NP in its framework or inside the pores of the MP oxides. For example, in a pioneering work by Stucky's group [23], an apparent difference in the reaction mechanism and a higher apparent initial activity were reported upon incorporation of Ag NP in TiO₂ MP films. Bannat et al. [24] demonstrated that Au can also improve the photocatalytic efficiency of TiO₂, with almost no difference between composites prepared by impregnation-reduction and electrochemical methods. They found that, for photocatalytic NO oxidation, the presence of Au NP and dendritic nanostructures in the pores of TiO₂ films substantially increases the photocatalytic activity by a factor of about 3 (from 15 to 40 % of the theoretical photon efficiency). A summary of these promising results is presented in Fig. 4.

3.2 Sensors

NP@MP composites have been tested as sensors of different kinds, taking advantage of diverse characteristics of the composites. For example, our group used NP@MP composite films to follow the evaporation of solvents from the pores, by simple spectroscopic monitoring of changes in the LSPR band of Au nanodecahedra covered with different MP films (Fig. 5a) [61]. By using this synthesis path, the NP remain accessible to solvents and, as a consequence, their LSPR band can be spectrally shifted as the effective refractive index varies during evaporation of the solvent initially wetting the mesopores, as shown in Fig. 5b, c. The evaporation profile can then be related to the boiling point of the solvent, type of film, and accessibility of the NP. Therefore, these NP@MP composites can

Fig. 4 *Left* Comparison of the photocatalytic activities of pristine and Au-loaded MP TiO₂ films as well as commercial Sto Photosan. *Right* Cross-section TEM micrographs and optical images of the composite films prepared by impregnation and chemical (Au NP) or electrochemical reduction (Au NW). Adapted with permission from [24]. Copyright 2009 American Chemical Society

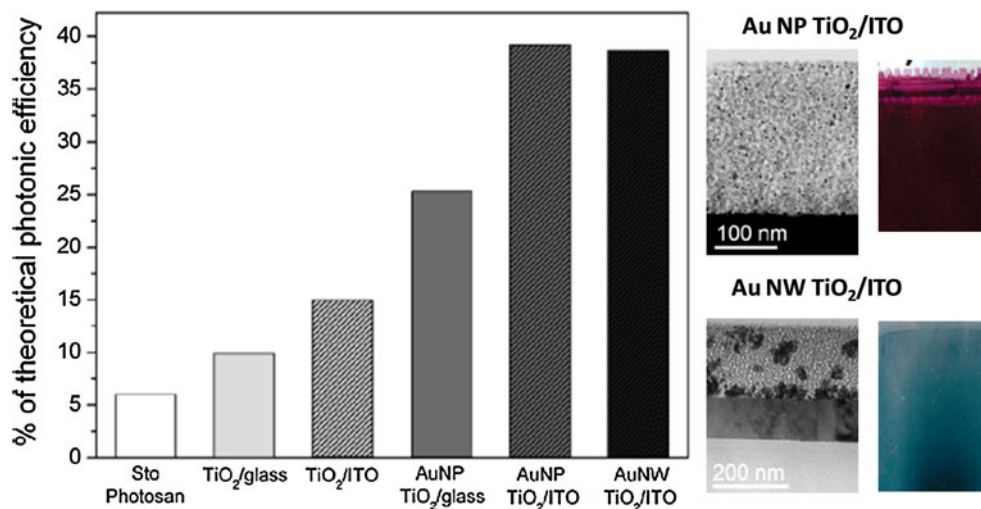
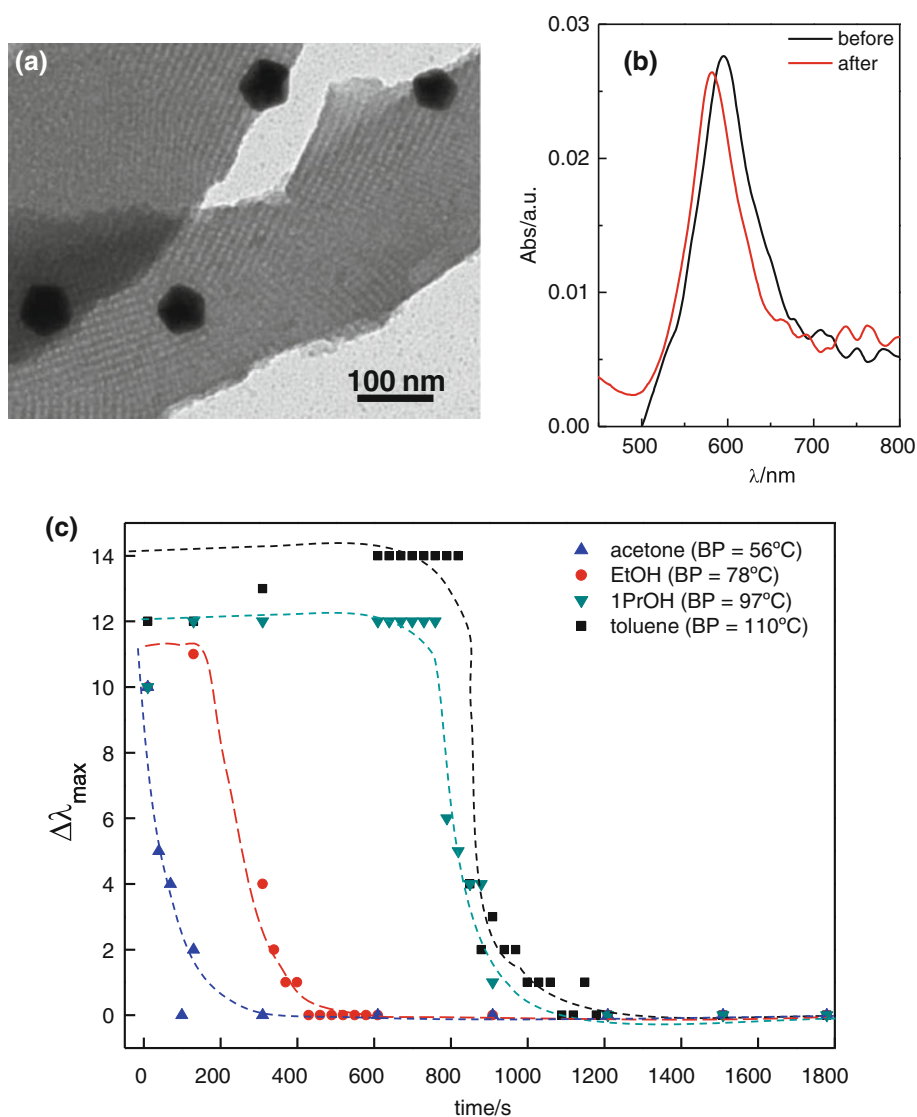


Fig. 5 **a** TEM image of Au decahedra covered with a SiO₂ MP film; **b** Spectra of the material shown in **a** before (black curve) and after (red curve) toluene evaporation. **c** $\Delta\lambda_{\max}(\text{LSPR})$ as a function of time, during the evaporation of different solvents. Lines are guides for the eye. Adapted with permission from Ref. [61] Copyright 2010 American Chemical Society (Color figure online)



be used to study the interactions between a solvent and an oxide thin film.

In a similar approach, Goettmann et al. [48] used Au NP (prepared ex situ and included in the sol just before film synthesis) embedded in MP SiO₂ films to detect organic molecules (PMe₃ and dodecanethiol) in solution, by following the LSPR band position. They also demonstrated that the system was selective toward small molecules, in principle due to the small pore size of the MP silica. Another recent application of the filtering ability of MP films has been reported, related to the exclusion of proteins from complex biological media, thereby facilitating the detection of small molecules by SERS [63]. In particular, 4-nitrobenzenethiol was clearly detected from a solution containing Bovine Serum Albumin (a usual serum protein) in buffer, without any contamination of the spectroscopic signal. In a related work, Malfatti et al. prepared SERS substrates from NP@MP composites [47] comprising the formation of metallic patterns inside the MP film by X-ray irradiation, so that a *lab on a chip* application can be envisioned for those composites. It is important to note that, although all these works are still closer to a proof-of-concept than to a real application, they are a promising first step of a novel approach that needs to be fully developed.

3.3 Optical properties

As discussed above, the preparation of NP@MP composites grants access to new properties due to the synergy between the components. In particular, the optical properties have been studied in detail, since they can have a key impact for the next generation of communication and information technology devices, as well as (bio)sensors and other biomedical products. We describe here a few selected studies regarding this subject.

3.3.1 Non linear optics

It has been demonstrated that NP incorporated in a dielectric matrix thin film present outstanding third-order optical nonlinearities [65]. These composites have been widely investigated due to their potential application in the next generation of optical communication and logical processing devices. Initially the composites were prepared by physical methods, such as co-sputtering, but suffered from drawbacks due to uncontrollable particle size and spatial distribution. Recently, several groups started to develop NP@MP thin film composites for non linear optics. By using these composites, it is possible to ensure a high dispersion and a good distribution uniformity of the NP in the films and thus, the nonlinear optical properties can be carefully controlled. With this approach, relatively

high third order nonlinear optical susceptibilities ($\chi^{(3)}$) were obtained, by using Au@MP TiO₂ [40, 66] and Au@MP SiO₂ composites [31, 32, 41]; and it was even possible to control the $\chi^{(3)}$ value by controlling the amount of Au incorporated in the matrix [32].

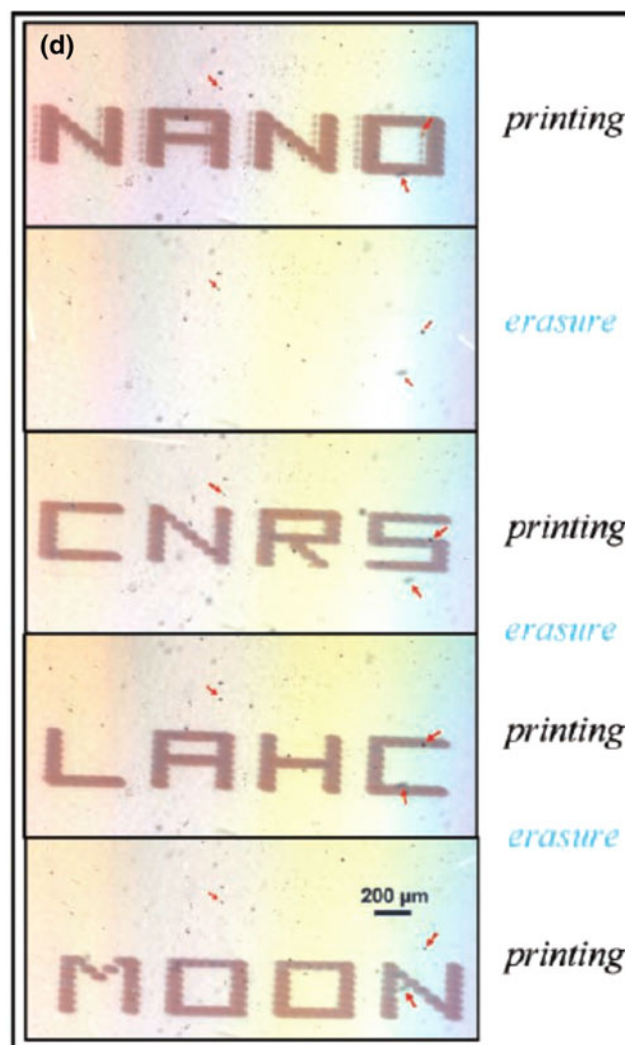
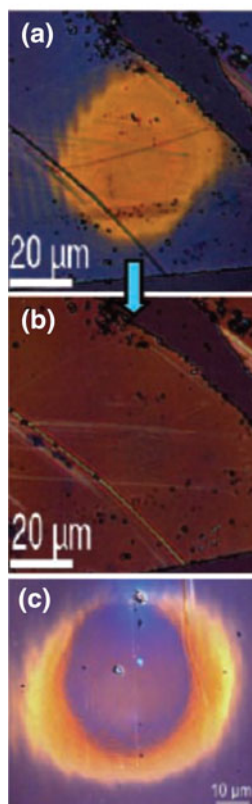
3.3.2 Photochromism

It is well known that photochromism (reversible change of color upon exposure to light) appears when Ag species interact with TiO₂. The process is similar to that described in the catalysis section above: under UV irradiation electrons at the valence band of TiO₂ are excited into the conduction band and then migrate toward Ag⁺ species, reducing them to Ag⁰. Then, the opposite reaction can occur: Ag NP interact with visible light through their LSPR and electrons migrate to the conduction band of TiO₂, which induces the oxidation of Ag⁰ to Ag⁺ [39]. The whole process is accompanied by a color change and therefore this property can be exploited in the design of optical data storage and display devices. The use of Ag@MP TiO₂ for this purpose was first demonstrated by Bois and collaborators in 2009 [39]. They observed the disappearance of the color associated to the LSPR band upon irradiation with visible light, which was then applied to “write” and “erase” Ag NP within MP TiO₂ by using UV and visible light (see Fig. 6). Interestingly, they found that at low irradiance, selective oxidation occurs leading to changes in the film color according to the wavelength used; whereas at higher irradiance, the oxidation of large NP is accompanied by the formation of many small NP in their vicinity, which provides the films with the same color for all tested wavelengths [35].

3.3.3 Emission enhancement

Noble metal NP can cause significant changes in the fluorescence behavior of adjacent fluorophores. This phenomenon is also present when the fluorophores are included within a MP matrix, and thus it has been measured for NP@MP composite films. As an example, Leroy et al. [67] demonstrated that the introduction of Ag NP can enhance the photoluminescence emission intensity of Eu³⁺ embedded in MP ZrO₂, probably due to energy transfer from Ag NP to Eu³⁺ or/and change of radiative decay rates. This is an interesting result, because these lanthanide doped ZrO₂ matrices are promising for optical amplification and light waveguides. Other groups have reported related results, such as rhodamine 6G photoluminescence enhancement (by a factor of 3) in Ag@Ti doped MP SiO₂ films [26] and fluorescence enhancement of organic fluorophores generated by Au nanorods embedded in MP SiO₂ films [55].

Fig. 6 **a** Ag dot printed onto a TiO₂ MP film by irradiation at 244 nm for 150 ms with an intensity below the threshold (30 kW cm⁻²) and **b** erased. **c** UV-printed dot (**a**) locally erased by a focused 488 nm-wavelength beam. **d** Words successively printed at 244 nm (30 kW cm⁻² for 150 ms) and erased at 488 nm at the same place. The films are observed in reflection with an optical microscope. Reproduced with permission from Ref. [35]. Copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim



3.4 Patterning

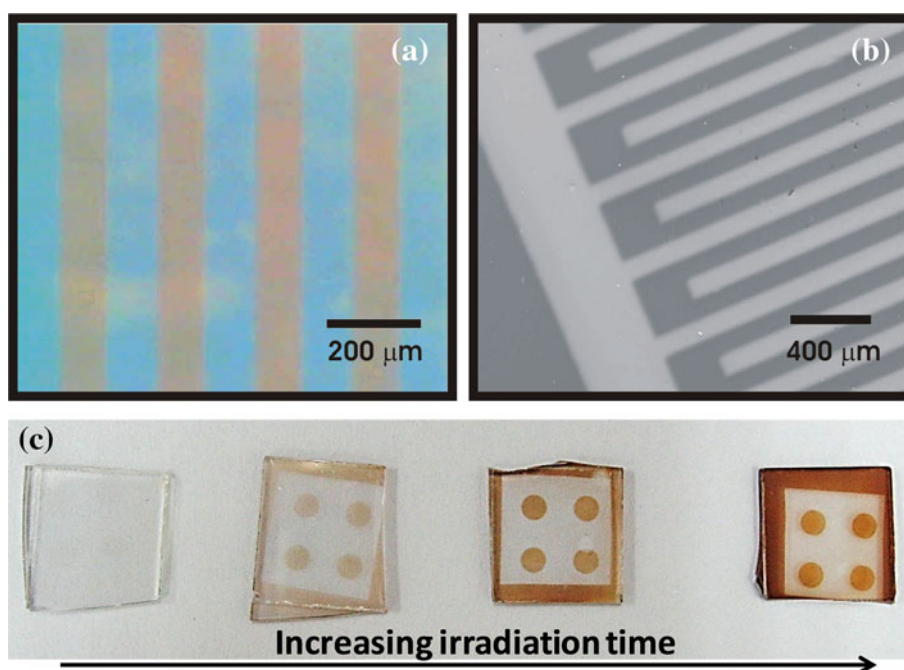
Au(III)@MP SiO₂ [50] and Ag(I)@MP SiO₂ [47] composites were synthesized by Innocenzi's group by means of a one-pot route. By Deep X-ray Lithography (performed in a synchrotron source), they managed to obtain metallic (Au or Ag) NP embedded within the film, only in the irradiated region. As X-rays also condense the inorganic framework, the method allows for the preparation of 3D MP structures onto a substrate. In a related approach, Martínez et al. [27] prepared Ag@MP TiO₂ composites by UV-exposure of Ag(I) impregnated MP TiO₂ using a conventional lithography mask. Patterns could be obtained (see Fig. 7) with arbitrary shapes in the submicron scale, rendering this method very powerful, as it is fully compatible with the techniques and substrates currently used in the sensors and microelectronics industry. Conductivity measurements [68] were performed in these composites and the results indicated a 3-dimensional connectivity between the embedded Ag NP.

Additionally, as described in Sect. 3.3.2 and shown in Fig. 5, it is also possible to create dot patterns by using irradiation with UV light without masks [35]. Despite only being the first steps, these studies pave the way toward the integration of MP films and NP@MP nanocomposites into real devices.

4 Outlook and perspectives

It is clear that the synthesis of NP@MP composite films is nowadays sufficiently well developed, and several methods are readily available to researchers. The variety of synthesis approaches offers several possible configurations, in which the composites may contain the NP inside the pores of MP oxides, but also included in the oxide framework or completely covered by the film. Interesting post-synthesis (templated) growth processes have also been devised, which allow exploiting the pore architecture to obtain new properties for the metallic component. Thus, the design of

Fig. 7 Reduction of Ag^+ by UV-light in TiO_2 MP films, using different masks to pattern the infiltration. **a** Optical image of the composite after 1 min of exposure. **b** SEM image of the sample shown in **a**. **c** Images of patterned composites, showing the increase in the amount of Ag incorporated as a function of irradiation time. **a** and **b** are reproduced with permission from Ref. [27], Copyright 2009 American Chemical Society



NP@MP composite films can be easily varied according to the desired application. Although the synthesis methods are settled and understood from the basic point of view, the applications of these composites are still under development. Several interesting seminal works have been presented and reviewed in this article, but a lot of work remains to be performed until useful devices are fully developed. Even though we have only discussed a few applications in catalysis and plasmonics, other fields may readily benefit from the special properties of these nanocomposites, such as environmental remediation or surface protection, among others. We expect that advancements in these areas and most probably many others will be reported in years to come.

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References

- Xia Y, Xiong Y, Lim B, Skrabalak SE (2009) Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? *Angew Chem Int Ed* 48(1):60–103. doi:10.1002/anie.200802248
- Daniel M-C, Astruc D (2003) Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem Rev* 104(1):293–346. doi:10.1021/cr030698+
- Schätz A, Reiser O, Stark WJ (2010) Nanoparticles as semi-heterogeneous catalyst supports. *Chem Eur J* 16(30):8950–8967. doi:10.1002/chem.200903462
- Astruc D, Lu F, Aranzas JR (2005) Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. *Angew Chem Int Ed* 44(48):7852–7872. doi:10.1002/anie.200500766
- Bohren CF, Huffman DR (1983) Absorption and scattering of light by small particles. Wiley science paperback series. Wiley-Interscience, New York
- Kreibig U, Vollmer M (1995) Optical properties of metal clusters. Springer series in materials science. Springer, Berlin
- Moores A, Goettmann F (2006) The plasmon band in noble metal nanoparticles: an introduction to theory and applications. *New J Chem* 30(8):1121–1132. doi:10.1039/B604038C
- Liz-Marzán LM (2006) Tailoring surface plasmons through the morphology and assembly of metal nanoparticles. *Langmuir* 22(1):32–41. doi:10.1021/la0513353
- Sepúlveda B, Angelomé PC, Lechuga LM, Liz-Marzán LM (2009) LSPR-based nanobiosensors. *Nano Today* 4(3):244–251. doi:10.1016/j.nantod.2009.04.001
- Alvarez-Puebla RA, Liz-Marzán LM (2010) SERS-based diagnosis and biodetection. *Small* 6(5):604–610. doi:10.1002/smll.200901820
- Atwater HA, Polman A (2010) Plasmonics for improved photovoltaic devices. *Nat Mater* 9(3):205–213. doi:10.1038/nmat2629
- Sperling RA, Rivera Gil P, Zhang F, Zanella M, Parak WJ (2008) Biological applications of gold nanoparticles. *Chem Soc Rev* 37(9):1896–1908. doi:10.1039/B712170A
- Doane TL, Burda C (2012) The unique role of nanoparticles in nanomedicine: imaging, drug delivery and therapy. *Chem Soc Rev* 41(7):2885–2911. doi:10.1039/c2cs15260f
- Grzelczak M, Pérez-Juste J, Mulvaney P, Liz-Marzán LM (2008) Shape control in gold nanoparticle synthesis. *Chem Soc Rev* 37(9):1783–1791. doi:10.1039/B711490G
- Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359:710–712. doi:10.1038/359710a0
- Sánchez C, Boissière C, Grosso D, Laberty C, Nicole L (2008) Design, synthesis, and properties of inorganic and hybrid thin

- films having periodically organized nanoporosity. *Chem Mater* 20(3):682–737. doi:[10.1021/cm702100t](https://doi.org/10.1021/cm702100t)
17. Soler-Illia GJAA, Sanchez C, Lebeau B, Patarin J (2002) Chemical Strategies to design textured materials: from microporous and mesoporous oxides to nanonetworks and hierarchical structures. *Chem Rev* 102(11):4093–4138. doi:[10.1021/cr0200062](https://doi.org/10.1021/cr0200062)
 18. Kresge CT, Roth WJ (2013) The discovery of mesoporous molecular sieves from the twenty year perspective. *Chem Soc Rev* 42(9):3663–3670. doi:[10.1039/c3cs60016e](https://doi.org/10.1039/c3cs60016e)
 19. Innocenzi P, Malfatti L (2013) Mesoporous thin films: properties and applications. *Chem Soc Rev* 42(9):4198–4216. doi:[10.1039/c3cs35377j](https://doi.org/10.1039/c3cs35377j)
 20. Wang Q, Shantz DF (2008) Ordered mesoporous silica-based inorganic nanocomposites. *J Solid State Chem* 181(7):1659–1669. doi:[10.1016/j.jssc.2008.06.015](https://doi.org/10.1016/j.jssc.2008.06.015)
 21. White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ (2009) Supported metal nanoparticles on porous materials. Methods and applications. *Chem Soc Rev* 38(2):481–494. doi:[10.1039/B802654H](https://doi.org/10.1039/B802654H)
 22. Brinker CJ, Lu Y, Sellinger A, Fan H (1999) Evaporation-induced self-assembly: nanostructures made easy. *Adv Mater* 11(7):579–585. doi:[10.1002/\(SICI\)1521-4095\(199905\)11:7<579::AID-ADMA579>3.0.CO;2-R](https://doi.org/10.1002/(SICI)1521-4095(199905)11:7<579::AID-ADMA579>3.0.CO;2-R)
 23. Andersson M, Birkedal H, Franklin NR, Ostomel T, Boettcher S, Palmqvist AEC, Stucky GD (2005) Ag/AgCl-loaded ordered mesoporous anatase for photocatalysis. *Chem Mater* 17(6):1409–1415. doi:[10.1021/cm0485761](https://doi.org/10.1021/cm0485761)
 24. Bannat I, Wessels K, Oekermann T, Rathousky J, Bahnmann D, Wark M (2009) Improving the photocatalytic performance of mesoporous titania films by modification with gold nanostructures. *Chem Mater* 21(8):1645–1653. doi:[10.1021/cm803455k](https://doi.org/10.1021/cm803455k)
 25. Besson S, Gacoin T, Ricolleau C, Boilot J-P (2003) Silver nanoparticle growth in 3D-hexagonal mesoporous silica films. *Chem Comm* 3:360–361. doi:[10.1039/b208357d](https://doi.org/10.1039/b208357d)
 26. Horiuchi Y, Shimada M, Kamegawa T, Mori K, Yamashita H (2009) Size-controlled synthesis of silver nanoparticles on Ti-containing mesoporous silica thin film and photoluminescence enhancement of rhodamine 6G dyes by surface plasmon resonance. *J Mater Chem* 19(37):6745–6749. doi:[10.1039/b910474g](https://doi.org/10.1039/b910474g)
 27. Martínez ED, Bellino MG, Soler-Illia GJAA (2009) Patterned production of silver–mesoporous titania nanocomposite thin films using lithography-assisted metal reduction. *ACS Appl Mater Interfaces* 1(4):746–749. doi:[10.1021/am900018j](https://doi.org/10.1021/am900018j)
 28. Nadar L, Sayah R, Vocanson F, Crespo-Monteiro N, Boukenter A, Sao Joao S, Destouches N (2011) Influence of reduction processes on the colour and photochromism of amorphous mesoporous TiO₂ thin films loaded with a silver salt. *Photochem Photobiol Sci* 10(11):1810–1816. doi:[10.1039/c1pp05172e](https://doi.org/10.1039/c1pp05172e)
 29. Plyuto Y, Berquier J-M, Jacquiod C, Ricolleau C (1999) Ag nanoparticles synthesised in template-structured mesoporous silica films on a glass substrate. *Chem Comm* 17:1653–1654. doi:[10.1039/a904681j](https://doi.org/10.1039/a904681j)
 30. Qi H, Shopsowitz KE, Hamad WY, MacLachlan MJ (2011) Chiral nematic assemblies of silver nanoparticles in mesoporous silica thin films. *J Am Chem Soc* 133(11):3728–3731. doi:[10.1021/ja110369d](https://doi.org/10.1021/ja110369d)
 31. Gu J-L, Shi J-L, You G-J, Xiong L-M, Qian S-X, Hua Z-L, Chen H-R (2005) Incorporation of highly dispersed gold nanoparticles into the pore channels of mesoporous silica thin films and their ultrafast nonlinear optical response. *Adv Mater* 17(5):557–560. doi:[10.1002/adma.200401085](https://doi.org/10.1002/adma.200401085)
 32. Lu Q, Cui F, Dong C, Hua Z, Shi J (2011) Gold nanoparticles incorporated mesoporous silica thin films of varied gold contents and their well-tuned third-order optical nonlinearities. *Opt Mater* 33(8):1266–1271. doi:[10.1016/j.optmat.2011.02.024](https://doi.org/10.1016/j.optmat.2011.02.024)
 33. Petkov N, Platschek B, Morris MA, Holmes JD, Bein T (2007) Oriented Growth of Metal and Semiconductor Nanostructures within Aligned Mesoporous Channels. *Chem Mater* 19(6):1376–1381. doi:[10.1021/cm0627239](https://doi.org/10.1021/cm0627239)
 34. Calvo A, Fuertes MC, Yameen B, Williams FJ, Azzaroni O, Soler-Illia GJAA (2010) Nanochemistry in confined environments: polyelectrolyte brush-assisted synthesis of gold nanoparticles inside ordered mesoporous thin films. *Langmuir* 26(8):5559–5567. doi:[10.1021/la9038304](https://doi.org/10.1021/la9038304)
 35. Crespo-Monteiro N, Destouches N, Bois L, Chassagneux F, Reynaud S, Fournel T (2010) Reversible and irreversible laser microinscription on silver-containing mesoporous titania films. *Adv Mater* 22(29):3166–3170. doi:[10.1002/adma.201000340](https://doi.org/10.1002/adma.201000340)
 36. Fukuoka A, Araki H, Sakamoto Y, Sugimoto N, Tsukada H, Kumai Y, Akimoto Y, Ichikawa M (2002) Template synthesis of nanoparticle arrays of gold and platinum in mesoporous silica films. *Nano Lett* 2(7):793–795. doi:[10.1021/nl0256107](https://doi.org/10.1021/nl0256107)
 37. Kumai Y, Tsukada H, Akimoto Y, Sugimoto N, Seno Y, Fukuoka A, Ichikawa M, Inagaki S (2006) Highly ordered platinum nanodot arrays with cubic symmetry in mesoporous thin films. *Adv Mater* 18(6):760–762. doi:[10.1002/adma.200502184](https://doi.org/10.1002/adma.200502184)
 38. Fuertes MC, Marchena M, Marchi MC, Wolosiuk A, Soler-Illia GJAA (2009) Controlled deposition of silver nanoparticles in mesoporous single- or multilayer thin films: from tuned pore filling to selective spatial location of nanometric objects. *Small* 5(2):272–280. doi:[10.1002/sml.200800894](https://doi.org/10.1002/sml.200800894)
 39. Bois L, Chassagneux F, Battie Y, Bessueille F, Mollet L, Parola S, Destouches N, Toulhoat N, Moncoffre N (2009) Chemical growth and photochromism of silver nanoparticles into a mesoporous titania template. *Langmuir* 26(2):1199–1206. doi:[10.1021/la902339j](https://doi.org/10.1021/la902339j)
 40. Cui F, Hua Z, Wei C, Li J, Gao Z, Shi J (2009) Highly dispersed Au nanoparticles incorporated mesoporous TiO₂ thin films with ultrahigh Au content. *J Mater Chem* 19(41):7632–7637. doi:[10.1039/B912016E](https://doi.org/10.1039/B912016E)
 41. Fang J-Y, Qin S-Q, Zhang X-A, Nie Y-M, Wang F (2012) Linear and nonlinear optical properties of gold nanocrystal-incorporated mesoporous silica thin films. *RSC Adv* 2(31):11777–11785. doi:[10.1039/c2ra21395h](https://doi.org/10.1039/c2ra21395h)
 42. Zhang Y, Yuwono AH, Li J, Wang J (2008) Highly dispersed gold nanoparticles assembled in mesoporous titania films of cubic configuration. *Micropor Mesopor Mater* 110(2–3):242–249. doi:[10.1016/j.micromeso.2007.06.009](https://doi.org/10.1016/j.micromeso.2007.06.009)
 43. Pérez MD, Otal E, Bilmes SA, Soler-Illia GJAA, Crepaldi EL, Grosso D, Sanchez C (2004) Growth of gold nanoparticle arrays in TiO₂ mesoporous matrixes. *Langmuir* 20(16):6879–6886. doi:[10.1021/la0497898](https://doi.org/10.1021/la0497898)
 44. Wu C-W, Yamauchi Y, Ohsuna T, Kuroda K (2006) Structural study of highly ordered mesoporous silica thin films and replicated Pt nanowires by high-resolution scanning electron microscopy (HRSEM). *J Mater Chem* 16(30):3091–3098. doi:[10.1039/b604062d](https://doi.org/10.1039/b604062d)
 45. Kanno Y, Suzuki T, Yamauchi Y, Kuroda K (2012) Preparation of Au nanowire films by electrodeposition using mesoporous silica films as a template: vital effect of vertically oriented mesopores on a substrate. *J Phys Chem C* 116(46):24672–24680. doi:[10.1021/jp308772b](https://doi.org/10.1021/jp308772b)
 46. Bois L, Chassagneux F, Desroches C, Battie Y, Destouches N, Gilon N, Parola S, Stéphan O (2010) Electroless growth of silver nanoparticles into mesostructured silica block copolymer films. *Langmuir* 26(11):8729–8736. doi:[10.1021/la904491v](https://doi.org/10.1021/la904491v)
 47. Malfatti L, Falcaro P, Marmiroli B, Amenitsch H, Piccinini M, Falqui A, Innocenzi P (2011) Nanocomposite mesoporous ordered films for lab-on-chip intrinsic surface enhanced Raman scattering detection. *Nanoscale* 3(9):3760–3766. doi:[10.1039/C1NR10404G](https://doi.org/10.1039/C1NR10404G)

48. Goettmann F, Moores A, Boissière C, Le Floch P, Sanchez C (2005) A selective chemical sensor based on the plasmonic response of phosphinine-stabilized gold nanoparticles hosted on periodically organized mesoporous silica thin layers. *Small* 1(6):636–639. doi:10.1002/sml.200500037
49. Battie Y, Destouches N, Bois L, Chassagneux F, Tishchenko A, SP Parola, Boukenter A (2010) Growth mechanisms and kinetics of photoinduced silver nanoparticles in mesostructured hybrid silica films under UV and visible illumination. *J Phys Chem C* 114(19):8679–8687. doi:10.1021/jp9046903
50. Malfatti L, Marongiu D, Costacurta S, Falcaro P, Amenitsch H, Marmiroli B, Greci G, Casula MF, Innocenzi P (2010) Writing self-assembled mesostructured films with in situ formation of gold nanoparticles. *Chem Mater* 22(6):2132–2137. doi:10.1021/cm902625v
51. Chassagneux F, Simon J-P, Bois L, Desroches C, Brioude A (2011) Reorganization induced by silver salt reduction inside a mesostructured block copolymer silica film. *J Phys Chem C* 115(51):25201–25208. doi:10.1021/jp207207x
52. Gu J, Shi J, Xiong L, Chen H, Ruan M (2004) A new strategy to incorporate highly dispersed nanoparticles into the pore channels of mesoporous silica thin films. *Micropor Mesopor Mater* 74(1–3):199–204. doi:10.1016/j.micromeso.2004.06.019
53. Krylova GV, Gnatyuk YI, Smirnova NP, Eremenko AM, Gun'ko VM (2009) Ag nanoparticles deposited onto silica, titania, and zirconia mesoporous films synthesized by sol-gel template method. *J Sol-Gel Sci Technol* 50(2):216–228. doi:10.1007/s10971-009-1954-x
54. Cortial G, Siutkowski M, Goettmann F, Moores A, Boissière C, Grosso D, Le Floch P, Sanchez C (2006) Metallic nanoparticles hosted in mesoporous oxide thin films for catalytic applications. *Small* 2(8–9):1042–1045. doi:10.1002/sml.200600154
55. Yang Z, Ni W, Kou X, Zhang S, Sun Z, Sun L-D, Wang J, Yan C-H (2008) Incorporation of gold nanorods and their enhancement of fluorescence in mesostructured silica thin films. *J Phys Chem C* 112(48):18895–18903. doi:10.1021/jp8069699
56. Kobayashi Y, Correa-Duarte MA, Liz-Marzán LM (2001) Sol-gel processing of silica-coated gold nanoparticles. *Langmuir* 17(20):6375–6379. doi:10.1021/la010736p
57. Pérez-Juste J, Correa-Duarte MA, Liz-Marzán LM (2004) Silica gels with tailored, gold nanorod-driven optical functionalities. *Appl Surf Sci* 226(1–3):137–143. doi:10.1016/j.apsusc.2003.11.013
58. May RA, Patel MN, Johnston KP, Stevenson KJ (2009) Flow-based multiadsorbate ellipsometric porosimetry for the characterization of mesoporous Pt–TiO₂ and Au–TiO₂ nanocomposites. *Langmuir* 25(8):4498–4509. doi:10.1021/la8038158
59. Mitra A, Jana D, De G (2012) A facile synthesis of cubic Im(-3)m alumina films on glass with potential catalytic activity. *Chem Comm* 48(27):3333–3335. doi:10.1039/c2cc18053g
60. Patel MN, Williams RD, May RA, Uchida H, Stevenson KJ, Johnston KP (2008) Electrophoretic deposition of Au nanocrystals inside perpendicular mesochannels of TiO₂. *Chem Mater* 20(19):6029–6040. doi:10.1021/cm8012705
61. Angelomé PC, Liz-Marzán LM (2010) Monitoring solvent evaporation from thin films by localized surface plasmon resonance shifts. *J Phys Chem C* 114(43):18379–18383. doi:10.1021/jp106528n
62. Angelomé PC, Pastoriza-Santos I, Pérez Juste J, Rodríguez-González B, Zelcer A, Soler-Illia GJAA, Liz-Marzán LM (2012) Growth and branching of gold nanoparticles through mesoporous silica thin films. *Nanoscale* 4:931–939. doi:10.1039/c2nr11547f
63. López-Puente V, Abalde-Cela S, Angelomé PC, Alvarez-Puebla RA, Liz-Marzán LM (2013) Plasmonic mesoporous composites as molecular sieves for SERS detection. *J Phys Chem Lett* 2715–2720. doi:10.1021/jz4014085
64. Muraza O, Rebrov EV, Berenguer-Murcia A, de Croon MHJM, Schouten JC (2009) Selectivity control in hydrogenation reactions by nanoconfinement of polymetallic nanoparticles in mesoporous thin films. *Appl Catal A* 368(1–2):87–96. doi:10.1016/j.apcata.2009.08.014
65. Hamanaka Y, Fukuta K, Nakamura A, Liz-Marzán LM, Mulvaney P (2004) Enhancement of third-order nonlinear optical susceptibilities in silica-capped Au nanoparticle films with very high concentrations. *Appl Phys Lett* 84(24):4938–4940
66. Cui F, Feng C, Xie R, Hua Z, Cui X, Zhou J, Wei C, Ohtsuka H, Sakka Y, Shi J (2010) Significant third-order optical nonlinearity enhancement of gold nanoparticle incorporated mesoporous silica thin films by magnetic field thermal treatment. *J Mater Chem* 20(38):8399–8404. doi:10.1039/c0jm00886a
67. Leroy CM, Cardinal T, Jubera V, Aymonier C, Treguer-Delapierre M, Boissière C, Grosso D, Sanchez C, Viana B, Pellé F (2013) Luminescence properties of ZrO₂ mesoporous thin films doped with Eu³⁺ and Agn. *Micropor Mesopor Mater* 170:123–130. doi:10.1016/j.micromeso.2012.11.014
68. Martínez ED, Granja L, Bellino MG, Soler-Illia GJAA (2010) Electrical conductivity in patterned silver–mesoporous titania nanocomposite thin films: towards robust 3D nano-electrodes. *Phys Chem Chem Phys* 12(43):14445–14448. doi:10.1039/C0CP00824A