Sol-gel engineering to tune structural colours

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Marco Faustini[1]*

[1]Sorbonne Université, CNRS, Collège de France UMR 7574 Chimie de la Matière Condensée de Paris, F-75005 Paris, France

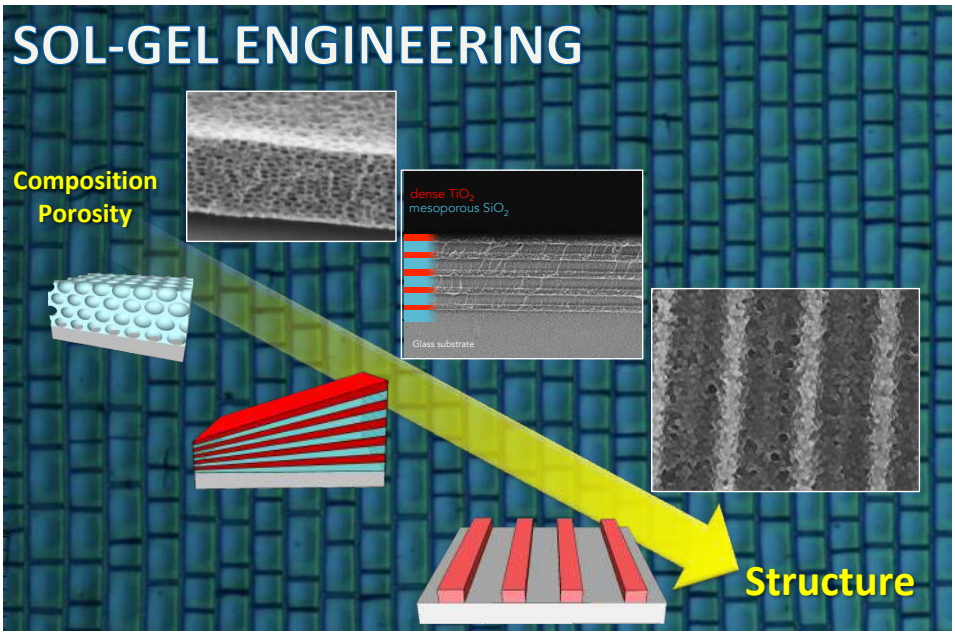
marco.faustini@sorbonne-universite.fr

Abstract

For several decades, the sol-gel process allows the fabrication of functional materials through the strong coupling between materials chemistry and advanced processing. This branch of material's science is generally associated to the formation of oxide and hybrid materials obtained through a transition between a sol and a gel. Engineering the sol-gel process to extend same principles to other classes of materials is an emerging and promising research line. These aspects will be illustrated in this article by reviewing the successful case of optical materials with tunable structural colors. It will be shown that sol-gel transition from molecular or colloidal building blocks results in optical materials with great diversity in structure and composition such as oxide, hybrid or, Metal Organic Frameworks. Applicative examples will be provided including photocatalytic, "invisible" and anti-reflective coatings, graded photonic mirrors and 2D photonic sensors.

Keywords
Sol-gel, MOFs, anti-reflection, crack self-assembly, diffraction gratings

Graphical abstract



1. Introduction

1.1. Better Ceramics through Chemistry, 30 years after

The legacy of Donald R. Ulrich concerns the rise of the sol-gel field that he promoted in the famous series of symposiums called "Better Ceramic through Chemistry"[1,2] These events marked the beginning of the sol-gel community[3]. At the time, he pioneered the so-called "ultrastructure processing" of glass-ceramic materials by chemical strategies. This approach was described by D. Ulrich in 1988, as chemical processing at the sub-micrometric scale based on molecular manipulation of various types of sols, gels, and organometallic precursors at low temperature that could eventually be converted to ceramic materials at more elevated temperatures[4]. After more than 30 years from Ulrich's perspective article, most of the key advantages of sol-gel in term of chemistry and processing are still valid today.[3] Since the very beginning, the sol-gel process is ideally suited to fabricate inorganic and hybrid materials with great control of the compositions, structuration and unbeaten versatility.[5] Notably, such inorganic polymerization at low temperature combined with soft-templating allowed the fabrication of mesostructured and mesoporous materials [6-8]. From a technological point of view, the sol-gel process undergoes a liquid-solid rheological transition allowing shaping of the inorganic materials very much as polymers [9]. The processing step can be applied at different stages: for instance thin films can be obtained by deposition process from the liquid sol [10,11]. Replication, molding, templating or shaping of inorganic materials are usually carried out on more viscous systems just before gelification [9]. Different shaping processes can also be combined giving rise to materials with sophisticated architecture that can be key components for new applications, at least for sol-gel materials.

Yet the concept of sol-gel goes now beyond the synthesis of ceramic materials by inorganic polymerization. In the last years, new sol-gel processing routes are emerging. According to IUPAC, the sol-gel is "a process through which a network is formed from solution by a progressive change of liquid precursor(s) into a sol, to a gel, and in most cases finally to a dry network"[12,13] . Consequently, in addition to what is generally assumed, materials obtained by a sol-gel process are not exclusively oxides or ceramics but can be carbon-based materials [14] or even Metal-Organic Frameworks (MOFs) [15]. This broader field, that an be defined as "sol-gel engineering"; it takes advantage of the 30 years old know-how of conventional sol-gel routes and emerging chemical/process engineering methods to extend those strategies to other class of materials.

In this article conventional and emerging sol-gel routes will be discussed by focusing on the successful case of optical coatings exhibiting structural colours. This is not meant to be a comprehensive review on the field of photonic sol-gel materials, excellent reviews can be found in the literature [16]. Rather, this article is an overview on recent accomplishments on how structural colours in thin films can be engineered to tackle some applicative challenges by mastering the sol-gel process starting from molecular but also from colloidal building blocks.

1.2. Sol-gel Optical Coating: Old Topic, Countless Opportunities

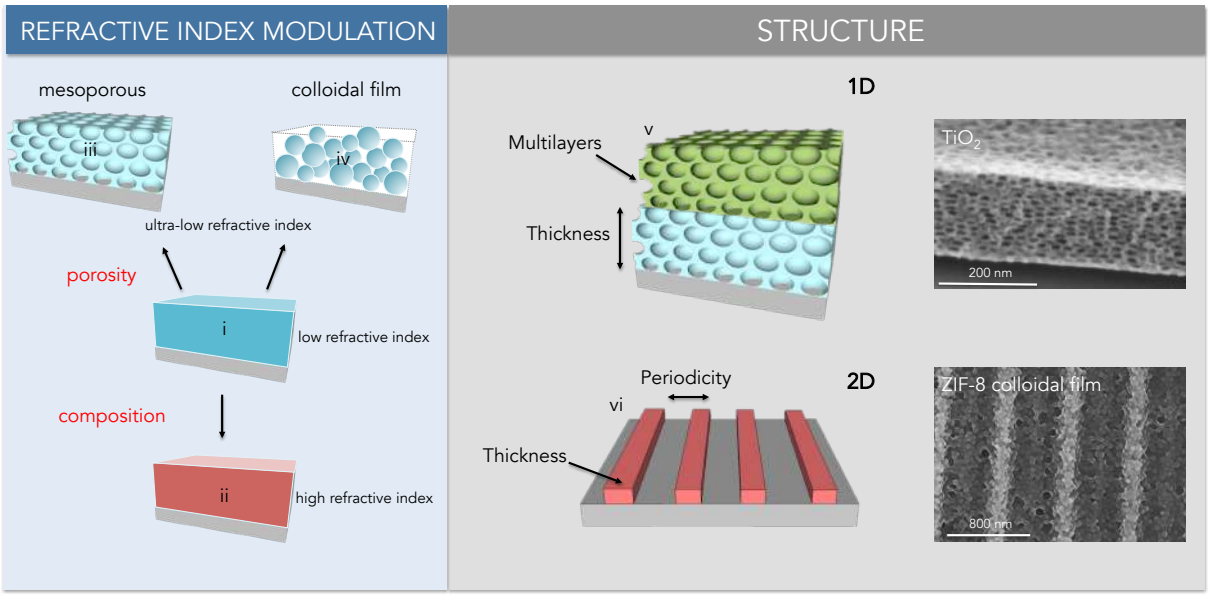


Figure 1 Conceptual illustration of the some general strategies associated to the molecular design and construction of functional sol-gel derived coatings with tunable optical properties: (i) low refractive index material, (ii) high refractive index material, (iii) porous material, (iv) colloidal films (v) 1D interferential coatings (vi) 2D photonic systems.

Since the very beginning of its long history, sol-gel process was identified as a promising technology for optical applications [17]. More than two decades ago, J. Livage et. al. describe the potential of sol-gel as " the ability to go all the way from the molecular precursor to the product, allowing a better control of the whole process and the synthesis of "tailor-made" materials "[18] . Curiously, the sol-gel technology driven by industrial needs was maybe developed before the sol-gel science. The first example on sol-gel optical coatings dates back to 1930 with the patent deposited from Geffcken and Berger from Schott Glaswerke Company. It describes the fabrication of oxide layers from metal oxide precursors by dip-coating [19]. The first products appeared on the market in 1953 and large scale production in 1959 with automotive rear-view mirrors, later anti-reflection coatings and sunshielding windows were introduced using TiO_2 and SiO_2 layers [20].

Despite its old history, sol-gel process still offers countless possibility to modulate optical properties [5]. Let's consider the case of a thin film. The optical performances depend on a combination of the intrinsic properties of the material and its structure. The sol-gel processing alone does not change the intrinsic properties of the materials. However, it offer new chemical strategies to assemble materials having unique structure at different scales [20]. To introduce the following part, some general strategies associated to the molecular design of coatings with tunable optical properties in the visible range will be described (Figure 1).

Refractive index modulation can be achieved by tuning the composition or adding porosity. Those heterogeneities must remain in the sub-wavelength range in order to consider the material as an effective medium. Let's focus on the case of "transparent" dielectric material that is not absorbing in the considered wavelength range. The simplest case is illustrated in Figure 1i); it corresponds to a sol-gel derived dense film with low refractive index, made of silica for instance. The best way to tune the refractive index of the material consists in changing the material's composition by modifying the initial synthetic conditions.

For instance, among the sol-gel materials, amorphous SiO_2 is considered a low refractive index material (n= 1.45 at 550nm) while nanocrystalline TiO_2 is a high refractive index material (n= 2.2-2.4 at 550nm) widely used in optical devices (Figure 1ii). Mixing two (or more) oxides such as SiO_2 and TiO_2 allows precise tuning of the refractive index of the coatings. For instance, amorphous and crystalline optical films made of binary SiO_2-TiO_2 can be obtained by co-condensation of Si and Ti oligomers [21]. Alternatively, nanocomposite networks with tunable optical density have been obtained by co-deposition of preformed TiO_2 nanocrystals and SiO_2 molecular precursors or particles [22].

The optical modulation of the refractive index can also be achieved by adding porosity in which the micro- or mesoporous layers can thus be seen as composite material composed by the inorganic phase and by air as illustrated in Figure 1(iii). Mesoporosity is formed from self-assembly of molecular or polymeric amphiphilic components coupled with polycondensation reactions or with other colloidal chemistry-based approaches [8,23]. The texture inducing process and the formation of the hybrid interface can be made by self-assembly of micelles, bridge hybrid precursors, lyotropic liquid crystals, or polymeric beads [24-28]. The porosity is obtained after the removal of the organic template by washing or by thermal treatment. Alternatively, nanoporous layers can be obtained by colloidal films (Figure 1iv), in which the void is localized in the inter-particles space. Colloids themselves can be porous as in the case of Metal-Organic Frameworks.

A unique feature of sol-gel materials is the capability to be shaped/combined periodically in order to "mold the flow of light" [29] by inducing structural colours thanks to interference, diffraction and photonic phenomena. In this category one can cite several kind of devices such 1D and 2D systems made, for example, of mesoporous materials or colloidal materials such as nanometric Zeolitic imidazolate framework 8 (ZIF-8) as shown in Figure 1 v and vi respectively. Here the structural colour will depend not only of the refractive index of the components but also on their structure at a larger scale in terms of thickness, periodicity, stacking, etc.. This is an extremely active field as evidenced by many important contributions reported in the last years from several groups [30-33].

In the following section, some recent examples of functional optical films developed in our group will be reported in which the structural colours were suppressed or induced to achieve specific functionalities.

2. Suppressing Structural Colours

2.1. "Invisible" photocatalytic coatings on glass

Glass is an outstanding material, massively employed in everyday life such as in optical devices, architecture, automobile and arts. Additional functionalities can be integrated in standard glasses by functional coatings. One topic of great interest concerns design multifunctional coatings on glass exhibiting several properties such as photoactivity, anti-reflectivity, mechanical resistance and, more even importantly, "invisibility". Why? Let's first illustrate this property with the example of photocatalytic coatings.

Photocatalytic coatings allow the glass surface to be "active" enabling decomposition of organic species under light irradiation [34,35]. They can be used for: (i) their self-cleaning capabilities, to decompose non-volatile organic species from the surface[36] preserving the surface appearance or (ii) air depollution of volatile organic compounds especially if they are

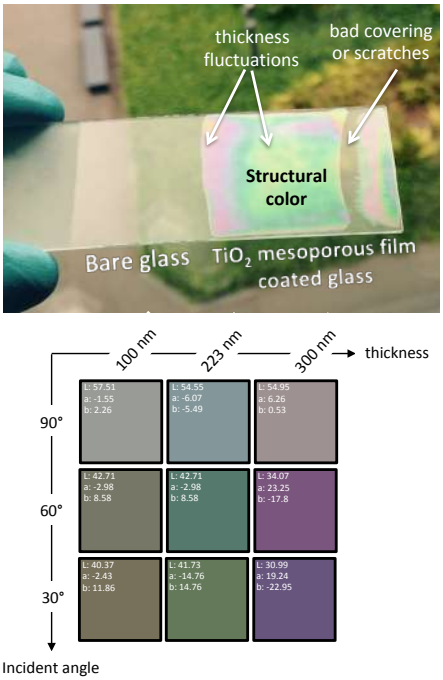


Figure 2 Structural colours on glass: (top) photograh and (bottom) simulation as function of the thickness and angle. Adapted from [37]

odorous and harmful [38-40]. To be applied on glass, an ideal coating must be highly photoactive with high surface area and with good mechanical, chemical and thermal stability. TiO_2 based mesoporous coatings have been considered as most serious candidates [41,42]. Optical quality nanocristalline TiO_2 mesoporous films can be obtained by sol-gel process in presence of templating agents [43,44] and can be easily applied by liquid deposition techniques [45].

However, porous photocatalytic films have not been applied yet in real applications. One of the main issues is the esthetical appearance of the coated-glass [46,47]. As illustrated in Figure 2, when the refractive index of the coating differs from the one of glass, structural colours are observed due interference phenomena taking place at the air/coating/glass interfaces [48,49]. Here structural colours are not suitable for design conception in many applications especially for architectural windows or automobile windshields. This (un) esthetical effect is even more problematic when the coating's thickness is not homogenous over the surface provoking colour fluctuation visible by naked eye [5] .

The "easiest way" to suppress the structural colors consists in matching the refractive index of glass all over the visible range of wavelengths. Due to the high refractive index of TiO_2 ($n \approx 2.4$) compared to glass ($n \approx 1.5$), one option to approach index-matching would consist in adding a low refractive index material, such as silica, in a TiO_2 porous network [50]. Mesoporous SiO_2 coatings containing preformed TiO_2 nanoparticles have been proposed by T. Gacoin's and later by Steiner's groups mainly to target photocatalytic properties [51,52] and anti-reflectivity.[36] However those interferential coatings always exhibit structural colours.

In a first example, photoactive invisible coatings obtained by mixing TiO_2, SiO_2 and air were designed by a rational approach based on simulation/experimental [37]. This approach can be described as follows: (i) measurement of the refractive index dispersion for each

component by spectroscopic ellipsometry; (ii) simulation of the reflected structural colours for different compositions by establishing 3-phases diagram (Figure 3); (iii) preparation of the "invisible coatings". Guided by simulation, photocatalytic TiO_2-SiO_2 mesoporous coatings were fabricated by one liquid deposition step process exploiting the evaporation induced self-assembled method using F127 block copolymer as an organic template mixed with TiO_2 and SiO_2 molecular precursors at various Ti/Si ratio. As revealed by Environmental Ellipsometric Porosimetry, Grazing-Incidence Small-Angle X-ray Scattering (GI-SAXS) and Grazing-Incidence Wide-Angle X-ray Scattering (GI-WAXS), addition of SiO_2 on TiO_2-based coatings results in a progressive porous network reconfiguration from "open" grid-like structure to more "isolated" spherical pores. As shown in Figure 3, only a precise combination of composition (60%TiO_2,40%SiO_2) and porosity (40%vol) allows obtaining invisibility, improved mechanical stiffness and high photocatalytic activity [53].

This can be observed in Figure 3 (right) showing the transmission curves for different thicknesses of the "invisible" layers that are nearly identical to the one of the bare substrate (as opposed to a typical mesoporous titania). Starting from the experimental transmission curves, the simulated reflected colours on "invisible" coatings present no shade, with a low dependency towards coating thickness and incidence angle. This is an important advantage in terms of processing because it allows obtaining "esthetical" photocatalytic coatings even in the case of thickness fluctuation during deposition. Thus low cost, larger scale deposition processes such as spray-coating can be considered.

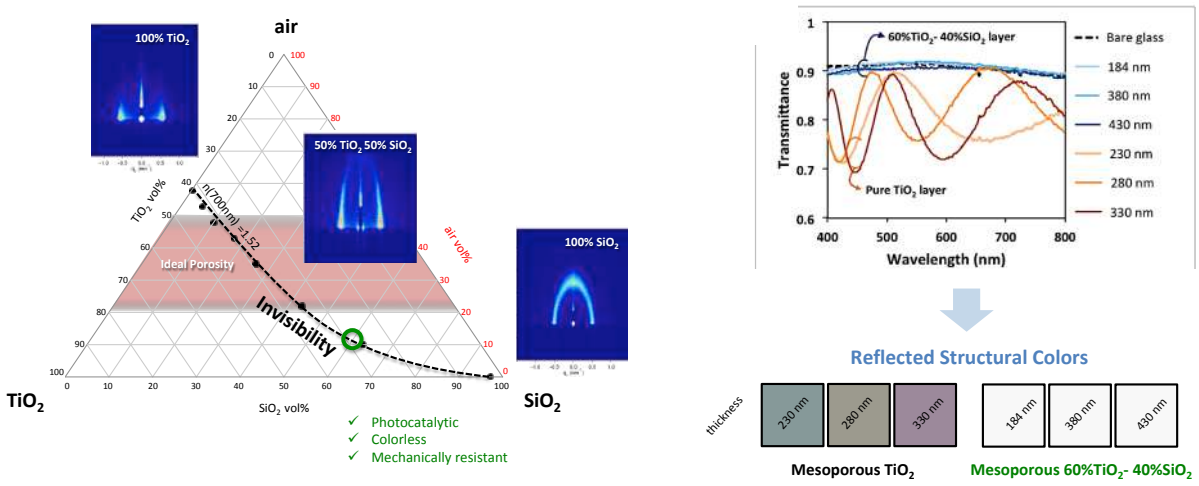


Figure 3 (left) 3-phases diagram and GI-SAXS patterns to follow the evolution of the refractive index and mesostrucure in SiO_2/TiO_2 porous composites (right) transmittance curves and simulated reflected colous of the "invisible" coatings. Adapted from [37]

2.2. Anti-reflective and photocatalytic coatings on glass

While glass is usually characterized by a high transmittance, another optical effect occurring at the glass/air interface is a partial reflection of light due to the refractive index contrast between the two media. This reflection is not technically considered as a structural colour, but is a common drawback for optical devices such as solar cells, automobile windshield or glass lenses. How to suppress reflection from photocatalytic coatings? A first approach consists in developing a single TiO_2 based multifunctional layer. An anti-reflective self-cleaning film deposited on glass would require a refractive index around 1.25. As mention above, TiO_2 refractive index is high (2.2-2.4) and reducing refractive index can be achieved by "adding" a large volume of porosity. This is challenging because a highly porous network generally collapses during crystallisation. This issue was overcome by developing an anti-reflective and photocatalytic crystalline TiO_2 layer with refractive index down to 1.27 and a hierarchical porosity up to 80% vol [54]. The great stability of the porosity upon thermal induced crystallisation and template removal was attributed to the combined effects of the presence of silica in the inorganic phase (10% mol) and the use of templates with different dimensions ranging from a few nanometers to 50 nm (PB-PEO, Pluronic F17, and PEG) [53]. The transmittance spectrum of the coated glass is reported in Figure 3 showing a characteristic V-curve and a gain in transmitted light of more than 3% (at 500 nm). While this coating is extremely appealing for its photocatalytic properties it presents some issues to meet industrial requirements: (i) due to the high porous volume this coating is mechanically fragile and (ii) water can be uptaken at low relative humidity by capillary condensation into the hydrophilic porosity increasing the refractive index of the film [35].

To prepare anti-reflective, photo-catalytic coatings and avoid water condensation, approaches based on multi-coatings were developed [55]. One example of antireflective, water-repellent, self-cleaning and anti-fogging multilayer is shown in Figure 4. The system is composed of a stack of two layers: (i) a hydrophobic, anti-reflective bottom layer composed by a methylated mesoporous silica film exhibiting water repellency and durable optical properties; (ii) an hydrophilic TiO_2 patterned top-layer acting as anti-fogging and self-cleaning film due to the capability of anatase to UV-decomposed organic compounds. The transmittance of the bilayer is plotted in Figure 4 together with the one of the ultraporous single layer detailed in previous example. While showing similar antireflective performances, the multilayer systems exhibit high mechanical, chemical and optical durability, making them serious candidates to be used as top antireflective coatings for photovoltaic cells or automobile for instance.

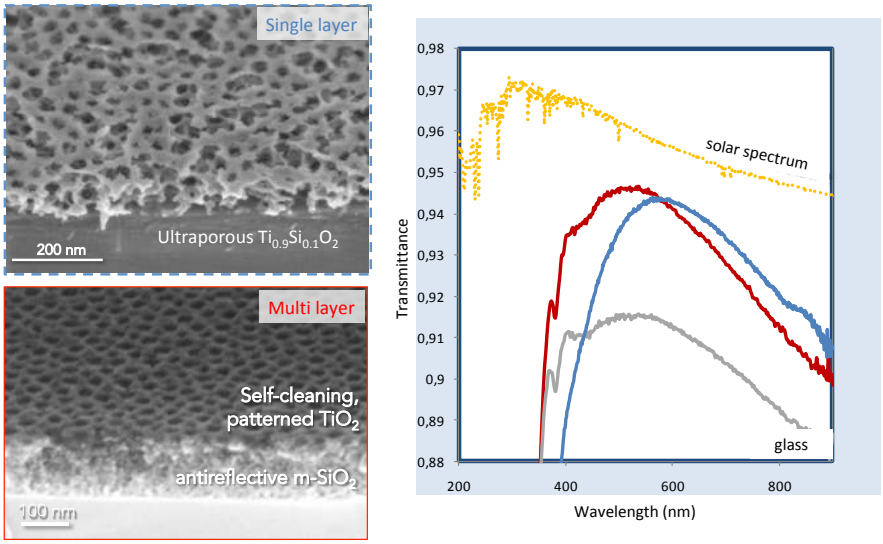


Figure 4 *Multifunctional photocatalytic anti-reflective coatings: single layer[54] vs multi layers strategies[55]*

3. Tuning Structural Colours

3.1. Graded 1D Photonic Crystals

To master the appearance of structural colours, the thickness of the coatings needs to be perfectly controlled. Spin-coating is widely used because it offers several advantages (single-side coating, low solution volume required). However, dip-coating is the first liquid deposition technique applied to sol-gel materials and probably the one that gives the best control in terms of thickness and evaporation rate. Several models have been proposed to predict the evolution of the thickness as respect to the withdrawal speed and temperature. At speeds above 1 $mm.s^{-1}$, the thickness-speed relationship can be described by the Landau-Levich model [56]. In 2010, a new "capillary regime" was described at speed below 0.1 mm s^{-1} for sol-gel systems obtained by hydro-alcoholic solutions. In this case, the deposition is governed by the evaporation of the solvent at the meniscus that drives a convective flow of the solutes from the solution to the triple point. This phenomenon is better known as "coffee-ring effect" observed in the case of evaporating colloidal droplets and evidenced by Deegan in 1997 [57]. In this configuration, the final thickness is proportional to the withdrawal speed at the power -1. Between the capillary and draining regime, an intermediate regime is located between 0.1 and 1 $mm.s^{-1}$ where the minimal thickness is obtained. A global semi-empirical predictive model was proposed taking into account both capillary and draining regimes.

Once established simple semi-empirical rules governing dip-coating deposition, other contributions were reported in the following years [58-61]. One example is the development of a new method called " dip coating in acceleration mode " to fabricate surfaces with gradients of properties [62]. Indeed graded surfaces can be useful in many technological domains such as for controlled wetting, combinatorial studies, tunable optics, aerospace, etc. and, of course, to tune structural colours.

Fabrication of surfaces with gradient of optical properties is challenging. How dip-coating can help?

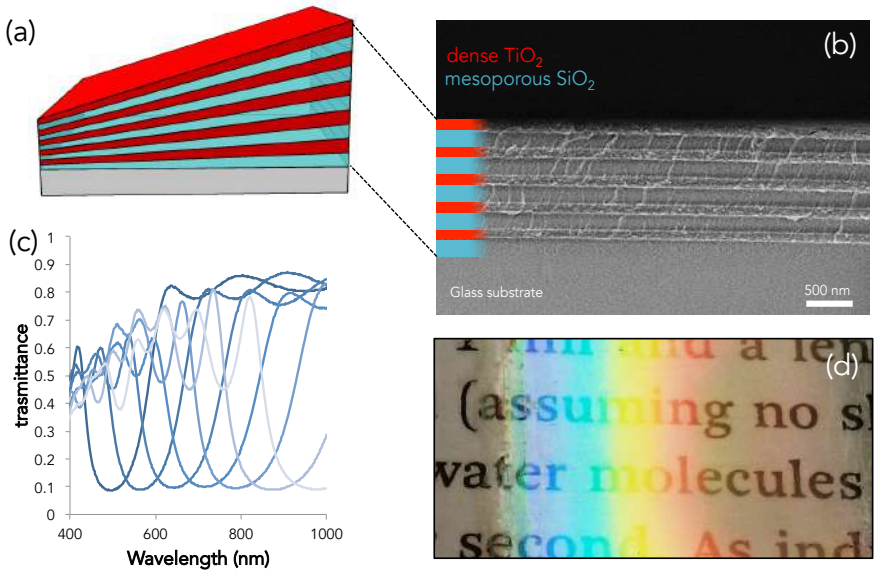


Figure 5 (a) Graded 1D photonic crystals made by dip-coating in acceleration mode, (b) cross-section SEM, (c) transmittance as function of the lateral distance (d) photograph of the device. Adapted from [62]

As mentioned before in a conventional dip-coating process the substrate is withdrawn from a solution at a constant speed; the final thickness depends on the value of the latter withdrawal speed. Now, if the dip speed is dynamically increased during dip coating (by accelerating) one can theoretically obtained films with variable thickness along the dipping direction. The influence of the speed variation on the thickness profiles was investigated unveiling the important roles played by the evaporation rate and by the viscosity on the fluid draining-induced film formation. Through this study, a semi-experimental equation to obtain on-demand thickness profiles was established [62].

By exploiting the dip-coating in acceleration mode, several example of graded devices could be demonstrated such as graded optical interferometry mirrors/filters, microfluidic channels with gradient in height, or surfaces with wettability gradient [62].

One interesting example concern 1D photonic crystals. In general, they consist of an alternating, high and low refractive index dielectric multilayer stack. To obtain higher reflectivity, one should (i) increase the refractive index contrast between low and high refractive index layers and/or (ii) increase the number of layers (typically at least 4 pairs). As discuss above low refractive index materials are SiO_2 (or even mesoporous SiO_2) while TiO_2 and ZrO_2 are often chosen as high refractive index materials. The optical thickness, nh of each layer equals $\lambda/4$, with λ being the wavelength for which Bragg reflection occurs, n the refractive index of the materials and h the layer thickness [16]. The position of the so-called 'stop-band' can be tuned by controlling the thickness of the layers.

Figure 5 illustrates, a 1D photonic crystals exhibiting a controlled lateral gradient in photonic stop-band. The system is made of 5 pairs of alternated low and high refractive index layers based on mesoporous SiO_2 and dense TiO_2 (Figure 5(a)). Both materials have been processed in order to obtain linear gradients.

A cross-section view of the multi-stack is displayed in the SEM micrograph in Figure 5b. The optical device on glass substrate acts as graded reflectors as demonstrated by the optical

photo in Figure 5(d). In particular, Figure 5(c) shows the transmission data of the systems taken at various dipping distance. In this example, the photonic stop-band can be displaced over a very wide range of wavelengths (from 470 to 960 nm) without variation in the minimum transmittance values (less that 10%). This kind of device can be potentially used as versatile optical filter or mirror in which the stop-band position can be easily tuned from UV to the Near InfraRed domains (depending on the absorption limits of all components) by simply displacing the light beam position over the surface. The same concept can be generalized to a wide range of lower or higher wavelengths. However fabrication of thicker stacks in the IR is more challenging due to the formation of cracks during annealing.

3.2. MOF-based Colloidal 2D Diffraction Gratings

As mentioned above, sol-gel process is not limited to molecular inorganic precursors undergoing inorganic polymerizations. Gelation of colloidal solutions can also be considered as a sol-gel process. Consequently "sol-gel engineering" to tune structural colours can be extended to other hybrid colloidal materials such as MOFs containing intrinsically micro-mesoporosity. Periodic materials exhibiting tunable structural colours can also thus be envisioned as photonic vapour sensors for instance. In this regard, the targeted materials are nanoporous materials such as sol-gel based micro or mesoporous materials or/and MOFs. Porous photonic structures are appealing for sensing applications,[63] for which the optical output relies on the change of refractive index in response to the analyte adsorption into the porosity [64,65]. Common photonic structures are Photonic Crystals made of periodic variation of optical density commonly in 1 or 3 dimensions. Considering the case of MOFs, some recent works demonstrated the integration of MOFs into photonic components such as thin films, [64,65] Fabry-Pérot,[66] 1D Bragg stacks,[67-69] or 3D colloidal crystals [70]. In all these examples, a gaseous pollutant uptaken into the pores provokes a change in the reflected colour.

One emerging class of photonic devices consists in the 2D porous Diffraction Gratings. They are optical components with a periodic structure, which splits and diffracts light into several beams travelling in different directions.

The sensing method relies on the evaluation of the diffraction intensity change, induced by the MOF refractive index variation, which can be simply detected by a CCD camera, as those integrated in simple smart-phones. Thanks to the angular dispersion generated by the grating, it is possible to monitor the intensity change on all the wavelenghts simultaneously with a camera. The example in Figure 6 shows a smart-phone assisted detection (at one wavelength) using ZIF-8 colloidal films as sensing materials. This MOF is particularly appealing since its porosity is hydrophobic and uptakes selectively organic pollutant but not water vapors (the main interferent in atmospheric sensing). In this specific example this selectivity was exploited to detect styrene vapors in humid atmosphere (a common « practical » problem in the chemical industry). The optical transduction was ensured by diffraction gratings based on TiO_2/ZIF-8 heterostructures obtained by direct Nanoimprinting Lithography of sol-gel films [71,72]. The detection of styrene down to 57ppm could be performed by a simple CCD camera and, interestingly, was based on the dynamic variation of diffraction intensity (rather than the absolute value) [50].

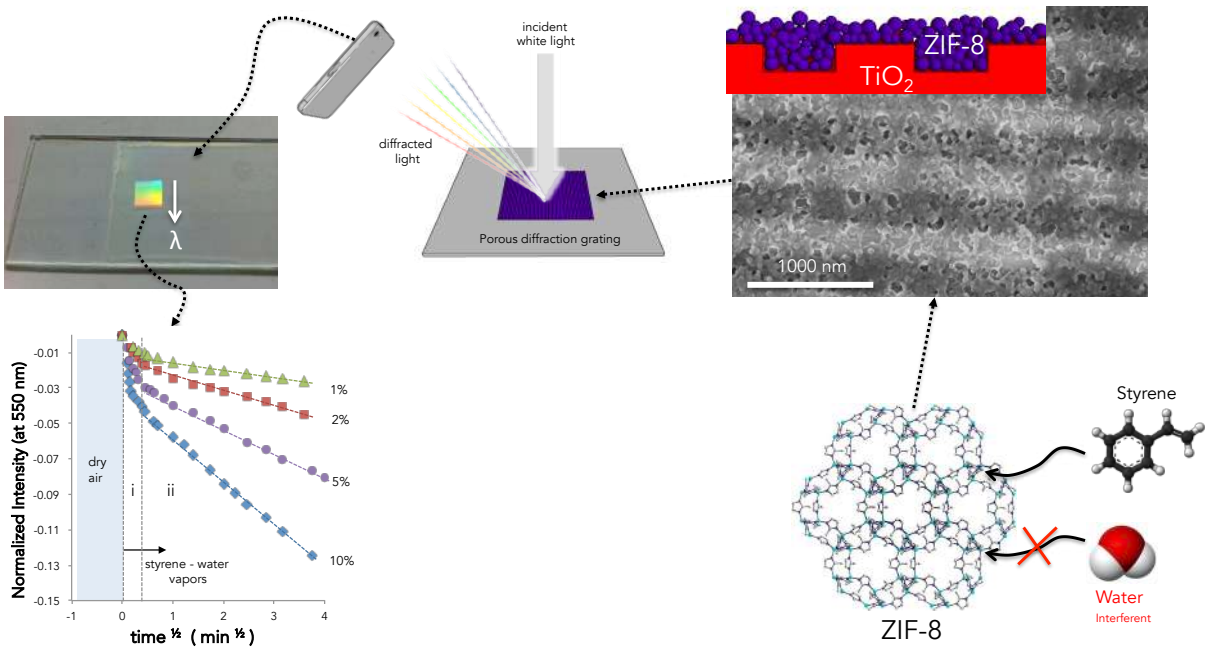


Figure 6 Nanoimprinted TiO_2/ ZIF-8 colloidal films act as vapor responsive diffraction grating. This configuration allows detection of volatile organic compounds by a simple CCD camera.

As mentioned before water vapor is detrimental for sensing organic compounds [73]. However, in specific conditions we can benefit of the presence of humidity to enhance the sensitivity of diffraction gratings sensors. One example is shown in Figure 7. In presence of small amount of ethanol, water capillary condensation can occur into hydrophobic mesopores leading to a significant increase of refractive index of the medium. Water condensation is triggered by the surfactant-like behaviour of alcohol molecules whose alkyl moieties preferentially interact with the hydrophobic walls and reversibly switch the surface energy from hydrophobic to hydrophilic [74]. This co-adsorption mechanism was exploited to enhanced sensitivity of the sensors made of hydrophobic mesoporous methylated SiO_2 diffraction gratings by direct imprinting of sol-gel films [75].

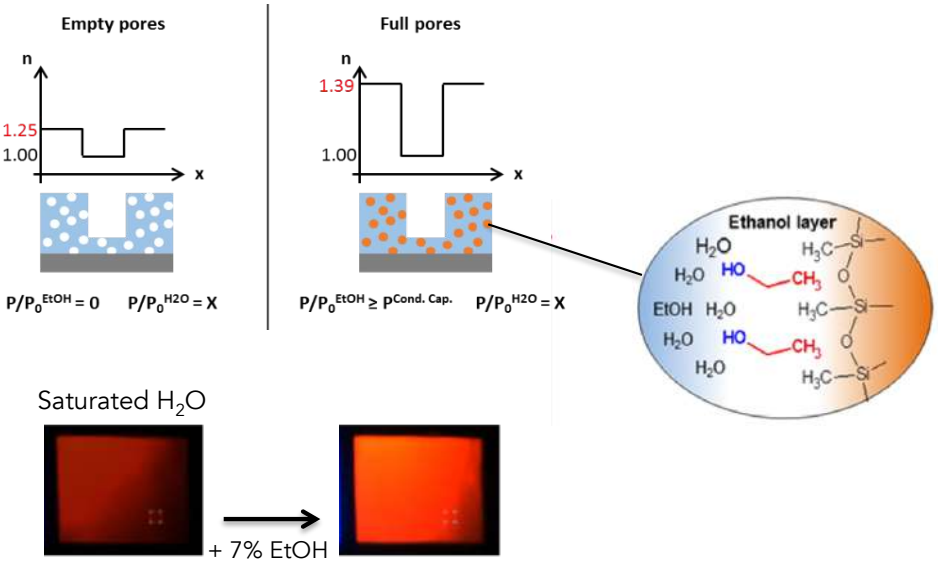


Figure 7 Mechanism of EtOH sensing based on water/EtOH coadsorption into porous hybrid silica diffraction gratings; adapted from **[75]**

3.3. Photonic Cracks

One of the common issues while fabricating colloidal films from liquid solutions is the formation of cracks. Crack nucleation and propagation in thin films is widely studied because of its ubiquitous appearance in gelation processes of colloidal suspensions occurring during drying in both natural systems such as mud or in artificial materials such as paint or nanoparticles films.

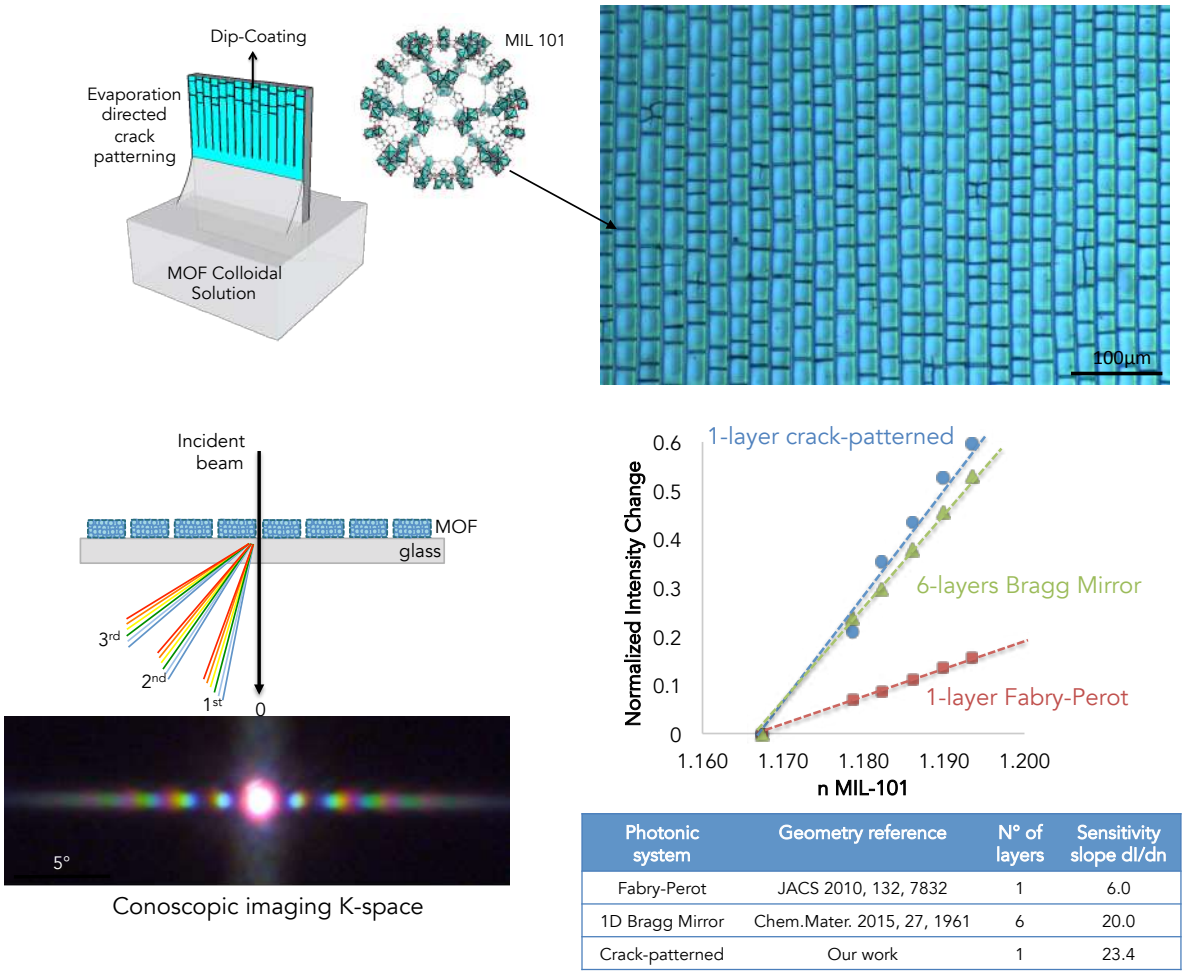
During drying, the colloidal gels slowly desiccate and shrink leading to an accumulation of internal stress that is released by crack nucleation and propagation. Noteworthy, in some cases, the propagation of the cracks throughout the film is not totally random; specific orientation and a structure composed of polyhedral patterns arises. Because the crack formation originates from the evaporation of the solvent from the suspension, drying in controlled conditions at slow evaporation rates such as the one encountered in the capillary regime (the "coffee ring" effect), gives a better self-organization of the cracks.

A promising approach consists in harnessing the formation of cracks in "coffee rings" by dip-coating in the capillary regime. The final goal is to develop a straightforward patterning method. Figure 8 (top-left) schemes the dip-coated assisted crack self-assembly approach. In the process, the substrate is first dipped into colloidal solution and withdrawn at low speed. During dip coating, three characteristic zones can be identified. The colloidal solution is located below the triple line. Just above the triple line, the nanoparticles form a "wet" colloidal gel made of percolating particles and filled with the solvent. Internal stresses start to accumulate because of the shrinkage provoked by solvent removal. In the "wet gel", regularly spaced cracks appear to release the evaporation-induced stress and then propagate perpendicularly to the drying line. Above the drying line, the solvent evaporates completely leaving a "dry-gel". The dried film is thus composed by an oriented, regularly spaced, microgrooves arrays.

As discussed, the fabrication of diffraction gratings can be done by approaches based on lithographic methods. While providing an excellent control, all these methods present critical drawbacks related to substrate geometry, scalability, versatility and/or cost.

Alternatively crack self-assembly can be an appealing « bottom-up » strategy to fabricate such 2D patterned structures. It has been demonstrated that Metal-Organic Framework colloidal films can be crack-patterned during dip-coating deposition where the crack propagation is oriented by the evaporation front [76].

Figure 8 (top-right) show an optical micrograph of the final systems that is composed of is a colloidal film composed by oriented, regularly spaced, brick-like micropatterns.



Photonic system	Geometry reference	N° of layers	Sensitivity slope dI/dn
Fabry-Perot	JACS 2010, 132, 7832	1	6.0
1D Bragg Mirror	Chem.Mater. 2015, 27, 1961	6	20.0
Crack-patterned	Our work	1	23.4

Figure 8 Evaporation Directed Crack Assembly of colloidal MOFs to fabricated photonic sensors. Adapted from [76]

Due to this high degree of order of the periodic structure in the direction perpendicular to the drying line, the crack-patterned MOF film diffracts light acting as diffraction grating. This dispersive capability of a crack-patterned MIL-101 films coated on glass was proved by Conoscopic Imaging in transmission mode performed using a microscope equipped with a Bertrand lens (Figure 8 bottom-left). Taking advantage of the high porosity and of the selective sorption properties of MIL- 101(Cr) and on the versatility of the crack-patterning process, a diffraction grating vapor sensors was developed. The signal transduction relies on the change of refractive index Δn in response to the vapor adsorption into the porosity as predicted by simple models proposed by Whitesides and co-workers [77,78] for gratings made of arrays of lines and is given in Equation (1):

$$\varphi = \frac{2\pi h(n_{MOF} - n_{air})}{\lambda} \qquad (1)$$

with φ representing the phase difference created when light passes through the MOF-based crack-patterns. The phase difference depends on the light wavelength λ, on the thickness h, and on the refractive index contrast between the colloidal MOF film (n_{MOF}) and the atmosphere (n_{air}=1).

The first order diffracted intensity can be deduced by Equation (2)

$$I_1 = \frac{2(1-\cos\varphi)}{\pi^2} \quad (2)$$

As a consequence, knowing n and h evolutions of the MOF material, the sensor response (dI_1/dn) can be maximized simply by controlling the thickness h. This property of diffraction gratings allows fabrication of sensors with "on-demand", enhanced sensitivity depending on the detection range [76].

The sensitivity performance (dI/dn) of the crack-patterned sensor has been compared through optical simulation to MIL-101 based Fabry-Perot and Bragg-Mirror sensors by adapting geometry and structural parameters from literature data and considering their best sensing configurations [66,69]. As detailed in Figure 7 (bottom-right), for a value of thickness that maximizes dI_1/dn, the crack-patterned sensor shows the best sensitivity that is comparable (and even higher) to the Bragg-Mirror system; this is remarkable considering that a Bragg-Mirror requires 6 steps of deposition of 2 different materials while crack-patterning can be realized in a single step. Beyond these performances, this study represents the first example of cracks harnessing for photonic applications with important implications from the applicative point of view.

4. Conclusions and perspectives

In this contribution, I reviewed some recent accomplishments in the fabrication of functional coatings with tuneable structural colours fabricated through "engineering" sol-gel strategies to conventional and emerging materials. In particular, suppression or appearance of structural colours was obtained by controlling the interplay between intrinsic optical properties of the materials and their structure. In this context, it was evidenced that sol-gel processing of (mesoporous) oxides from conventional molecular routes is perfectly suited to control composition, porosity and structure, especially when coupled with nanofabrication methods. This is a mature field that is now ready to solve great issues for challenging optical applications. For instance, an approach based on the direct nanoimprinting of sol-gel films has recently permitted to design a light trapping device exhibiting extremely high efficacy in ultrathin solar cells [79].

Importantly, following the same principles, sol-gel processing can be exploit starting from colloidal building blocks to shape photonic materials, by crack self-assembly for instance. The example of colloidal Metal-Organic Framework photonic surfaces was shown as practical case to prepare vapour sensors. This is extremely interesting for the evolution of the sol-gel field and to extend these strategies to other class of materials. For instance, in a recent article, simultaneous colloidal and molecular gelation has been exploited to fabricate highly porous metallic structures [80]. In general, it is believed that taking advantage of the versatility of the sol-gel process by extending the composition threshold (beyond oxides) is an exciting future research line for the field.

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Conflict of interest

The author declares that he has no conflict of interest.

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