Full Processing of Colloidal Photonic Crystals by Spin-Coating

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ABSTRACT

Herein we present different results on the application of spin-coating to the processing of thin films made of spherical colloids ordered in three dimensional structures. We focus on the infiltration and controlled introduction of optical planar defects. We show that the use of spin-coating largely diminishes the processing time scales typically used in the field of colloidal crystals, and still allows one to attain high quality structures. We demonstrate that spin-coating permits the controlled infiltration of colloidal crystals with many different types of compounds. Examples are given for different oxide and polymer guest compounds introduced in the voids of the colloidal lattices. Both scanning electron microscopy and optical spectroscopy evidence of such control are provided. We also show that a thin layer of particulate material can be spread onto a colloidal crystal by spin coating a suspension of such particles in which control over the aggregation state has been achieved first. This gives rise to a capped lattice that present surface resonant modes and can be used to build a planar defect embedded in the bulk. In all cases, evidence of the optical quality of the different samples made is provided.

Keywords: Colloidal crystal, spin-coating, processing, infiltration, planar defect.

1. INTRODUCTION

Colloidal crystals are often used as templates to impose three dimensional order at the micron length scale to oxides, semiconductors, metals, and polymers. In a typical procedure, a lattice made of silica or polystyrene colloidal spheres is infiltrated with a guest compound or its precursors, which inherits its periodicity. In most cases, a negative replica of the original porous solid may be attained by elimination of the matrix. Both the infiltration conditions and the chemical, thermal and mechanical stability of the guest material determine the choice of the appropriate template. So, polystyrene colloidal crystals are commonly used to mould oxides, since the former can be eventually dissolved or calcined with minimum distortion of the infiltrated material. In the case of polymers or semiconductors, whose synthesis usually involves high temperatures, ordered silica colloids are preferred as scaffolds, for they present high thermal stability and can be etched away by a selective hydrofluoric acid attack. Most of this work has been carried out within the field of photonic crystals. In this framework, there is a continuing interest in developing infiltration techniques that preserves the optical quality of the original lattice and, at the same time, that allows control over the filling fraction of the guest compound, since this in turn implies control over the optical properties of the composite. Compatibility with current optical or electro-optical device fabrication technology, low cost and simplicity are also features to be valued when a new infiltration technique is introduced.

In a further step towards functionalization, the development of techniques to introduce defects within colloidal photonic crystals in a controlled manner has also attracted great interest. This attention was caused by the potential technological applications resulting from the optical properties associated to defect state modes carefully engineered in the photonic gap of such lattices. Regarding planar defects, a few successful approaches have been taken up to date. A layer of spheres of an arbitrary diameter can be introduced within the bulk of an opal by combining colloidal crystal planarization and Langmuir-Blodgett techniques. A combination of convective self assembly and chemical vapour deposition has been used to create a silicon oxide slab sandwiched between two opal films. In this approach, the starting opal film must be infiltrated with a guest compound until the entrance pores are closed, thus allowing the deposition of a coating of the desired thickness on the lattice surface. Afterwards, a new colloidal crystal is formed on top of the coating and also infiltrated in order to present a similar composition than the starting opal. A transfer printing technique has also been successfully employed to place a polymer multilayer of controlled thickness on top of an opal...
The optical effects associated to the presence of defects, such as sharp dips (peaks) observed in the reflectance (transmittance) spectra at stop band frequencies, are stronger in the latter case than in previous ones. The reason for that is that the use of transfer printing permits to build polymer defect layers without infiltrating the surrounding opal films, as it happens when CVD is used to grow oxide planar defects, which largely diminishes their photonic strength.

In section 2, the preparation of the base materials employed in our studies, thin colloidal crystal films, is described. We employed the well-known evaporation induced self-assembly (EISA) deposition technique developed by Colvin et al.\textsuperscript{18}

In section 3, we demonstrate that spin coating, a widely employed technique to deposit polymer thin films on semiconductor wafers in microelectronics, can be also used to create a continuous film of controlled thickness of a wide range of materials onto the surface of colloidal spheres arranged in a three dimensional structure. We present results on the structural and optical properties of polystyrene, dense silica, mesoporous silica, and titania infiltrated within latex and silica colloidal crystal templates, as well as on the inverse colloidal crystals obtained from them, which exemplify the versatility of the method herein proposed. In all cases, the filling fraction of the guest compound can be precisely determined, hence providing control over the optical properties with unprecedented accuracy. The optical quality of the so obtained lattices is assessed from comparisons of the measured photonic crystal properties with theoretical predictions.

In section 4, we present a fast, reliable and accurate procedure based on spin coating to create two dimensional inorganic defect layers in artificial opals preserving the photonic strength of the lattice. The planar defect is formed by small aggregates of nanocrystalline colloids and can be built up of a wide variety of materials. Accurate control of the defect thickness is achieved, which yields control over the spectral position of the defect state introduced in the pseudogap of the colloidal crystal. This defect mode causes the opening of a narrow higher transmission window that can be accurately tuned during the synthesis.

### 2. PREPARATION OF THIN COLLOIDAL PHOTONIC CRYSTAL FILMS

The three dimensional macroporous substrates on which the spin coating infiltration process was performed were thin (from 5 to 10 micron thick), planarized colloidal crystals grown on glass slides by the above mentioned EISA technique.\textsuperscript{18} Briefly, a suspension of silica or polystyrene microspheres (average particle diameters ranging from 300 nm to 600 nm) in ethanol or mixtures of ethanol and water is let to evaporate while the substrate is vertically placed in the beaker. Convection and capillary forces acting on the particles at the meniscus between the substrate surface and the suspension give rise to highly crystalline films.

The introduction of planar defects was carried out within colloidal crystal films made of spherical polystyrene (PS) beads. The growth of colloidal crystals from polystyrene colloids in deionised water was carried out using a variation of the EISA method. For this purpose, commercial PS colloidal particles (IKERLAT) with an average diameter of 720 nm were employed.

\begin{figure}[h]
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\caption{(a) SEM image of a cross section of a polystyrene sphere thin colloidal crystal film. (b) The corresponding specular reflectance spectrum.}
\end{figure}
(polydispersity about 3%) were used. Substrates employed were glass microscope slides (12 mm x 76 mm), which were cleaned with doubly distilled water, acetone, carbon tetrachloride and with a 4:1 volume ratio H₂SO₄/H₂O₂ solution before being dried with a N₂ flow. These substrates were dipped into a cylindrical glass beaker (inner diameter, ca. 25 mm; volume, 25 mL) containing the PS colloidal suspensions (15 mL) with a concentration of 0.04% wt. Then, the beakers were placed in an oven at 50ºC and water was evaporated at a rate of 0.22 mm/h for 3 days, a high quality colloidal crystal being formed on an area of 12 mm x 16 mm of the substrate.

Figure 1 (a) shows a scanning electron microscopy (SEM) picture of a cross section of a colloidal crystal film. A specular reflectance spectrum of a thin colloidal crystal film is also shown in Figure 1(b). Optical characterization was performed using a Fourier Transform Infrared Spectrophotometer (BRUKER IFS-66) attached to a microscope and operating both in reflection and transmission mode. For reflectance measurements, a X4 objective with a numerical aperture of 0.1 (light cone angle ±5.7º) was used to irradiate the sample and collect the reflected light at quasi-normal incidence with respect to the (111) planes of the colloidal lattice. A spatial filter was used to selectively detect light from 0.1 mm² circular regions of the sample. A clear maximum corresponding to the Bragg diffraction due to the periodicity in the [111] direction can be seen, as well as Fabry-Perot oscillations arising from the interference of the light beams reflected at the top and the bottom interfaces of the thin film.

3. SPIN-COATING INFILTRATION

Figure 2. Scheme of the spin coating infiltration process. (a) First, a drop of the precursor fluid containing either the reactants, the guest compound dissolved or a suspension of nanoparticles is let to infiltrate the colloidal lattice. (b) Then, the substrate is spun at high speed causing thinning of the coating layer and evaporation of the liquid in the precursor. (c) Finally, a thin continuous layer of the guest compound is formed onto the spheres’ surface.

A scheme of the spin coating infiltration process described in this section is shown in Figure 2. The black chains drawn in the Figure can be thought of as polystyrene dissolved in toluene, a solution often used as a model to study polymer film formation by spin coating on wafers.¹⁹ Such precursor has already been used to infiltrate, by a different procedure, 3D macroporous silica colloidal crystals in order to create an inverted structure that could serve in turn as a template for the synthesis of a wide variety of colloids of spherical shape.²⁰ As in a standard spin coating infiltration process, we studied the possibility to tune the features of the composite through several parameters, such as the precursor solution concentration, the spinning speed, and the number of cycles performed. On the other hand, different types of oxides were synthesised within the interstitial voids of colloidal crystals by a similar procedure, to prove the generality of the procedure. Oxide infiltration is usually achieved by soaking the colloidal lattices in alcohol solutions of metal alkoxide precursors.¹ Later hydrolysis and condensation yields the metal oxide within the periodic porous matrix. Dip-coating and colloidal crystallization in the presence of oxide nanoparticles have also been employed. These methods yield large or complete infiltration of the pore volume, undesired external surface cappings being attained in many occasions. Besides, it does not permit control over the filling fraction or the location of the infiltrated oxide. Much more accurate control can be attained by alternate chemical vapor deposition (CVD) of metal chlorides and water on the particles surface where they react to form a thin coating whose thickness can be controlled with the number of cycles or amount of deposited reactants.¹⁶ Here, we used silicon tetramethoxide dissolved in methanol and titanium tetraethoxide dissolved in ethanol as precursors to infiltrate to spin coat dense SiO₂ and TiO₂, respectively, onto the micro-spheres’ surface. Also, we spin coated an ordered mesoporous sol-gel precursor to create a hierarchical material with order at two
different length scales. The precursor was prepared following a similar procedure to that previously reported to attain continuous mesoporous films.\textsuperscript{21} Pluronic F-127, a triblock copolymer, was used as structuring agent to yield a hybrid organic-inorganic mesoporous network. Full details are given in reference [22].\textsuperscript{22} In Figure 3, we show SEM images of inverse colloidal lattices made of (a) mesoporous silica, (b) dense titania, and (c) polystyrene, which demonstrate that the guest materials form a continuous thin coating of the three dimensional particle network. All these inverted lattices have been made by the spin coating infiltration procedure herein proposed. The drying and curing kinetics of the different guest compounds determine the mechanical stability, since cracks may appear at that stage.

![Figure 3](image)

**Figure 3.** SEM images of cross sections of different inverse colloidal crystals made by spin coating infiltration of a precursor solution of the guest compound and later removal of the original template. (a) Mesoporous silica; (b) Dense titania; (c) Polystyrene.

Since the level of infiltration of a certain compound is specifically related to a change in the position, intensity and width of the main reflection peak of the photonic colloidal crystal substrate, the optical properties of the samples can be used to monitor the colloidal crystal loading process. A microspectroscopy set up was employed to map the whole film surface. 1 mm\textsuperscript{2} areas were analysed using an FT Vis-NIR spectrophotometer attached to a microscope (X4 magnification objective). The effect on the optical specular reflectance of carrying out gradual spin coating infiltrations of a solution containing 20\% wt. polystyrene in toluene within a silica opal is shown in Figure 4(a). An example of cyclic infiltrations is also given for mesoporous silica infiltrated within a polystyrene lattice in Figure 4(b). In that case, a solution

![Figure 4](image)

**Figure 4.** (a) Specular reflectance spectra of the same thin silica colloidal crystal film after different number of infiltrations with polystyrene, performed by spin coating a solution of such compound in toluene. (b) Specular reflectance spectra of the same thin polystyrene colloidal crystal film after a different number of infiltrations with mesoporous SiO\textsubscript{2}, performed by spin coating a precursor solution in ethanol (see reference [22] for details). (c), (d), and (e) show the variation of the filling fraction of polystyrene in a silica colloidal crystal using different relevant parameters of the spin coating process as controlling factors, namely, the weight concentration of polystyrene, the number of infiltrations performed for the 20\% wt. solution, and the rotation speed, given in revolutions per second (rps), for that same precursor solution.
containing 8.83 g of ethanol, 0.69 g of water and 0.1 g of a 1M HCl aqueous solution was first prepared. 0.46 g of Pluronic F-127 (SIGMA-ALDRICH) was then added under stirring until a clear solution is formed. Finally, 1.0 g of TEOS (98%, MERCK) was then added drop-wise under stirring. The solution was then stirred at 80 ºC for 1 hour, in a flask provided with a condenser. Overall molar gel compositions was 1 TEOS: 9.2 H2O: 0.02 HCl: 40 EtOH:7.2x10⁻³ Pluronic F127. In Figures 4(c), 4(d), 4(e), we show that control over the filling fraction of the guest compound can be achieved through any of the aforementioned parameters for the case of polystyrene infiltrated in silica. As expected, the higher the concentration of the precursor solution (C₀), the slower the spinning the speed (ω), or the larger the number of cycles performed (N), the thicker the film deposited onto the spheres’ surface.

4. NANOCRYSTALLINE DEFECTS BY SPIN-COATING

In this section we present a fast and reliable method to create a 2D inorganic defect layer within colloidal crystals preserving the photonic strength of the lattice. The planar defect is formed by small aggregates of nanocolloids and can be made of a wide variety of materials. Control of the defect thickness is attained, which yields control over the spectral position of the defect state introduced in the pseudogap of the crystal. This defect mode causes the opening of a narrow higher transmission window that can be accurately tuned during the synthesis. Full details can be found in reference [23].

Figure 1 displays a diagram of the procedure employed to build up the colloidal heterostructures. A suspension containing oxide crystallites is deposited and spun onto a planarized self-assembled colloidal crystal in order to create a uniform nanocrystalline slab on top of it (drawings (a), (b), and (c) in Figure 5). Subsequent growth of a new colloidal crystal on top of the nanocrystalline layer gives rise to a heterostructure in which the translational symmetry is disrupted by the presence of the slab. The key parameter to control the formation of an external layer and prevent infiltration is to control the aggregation state of the nanoparticle suspension.

Figure 5. Scheme of the deposition of a thin capping layer onto a colloidal crystal by spin coating. (a) First, a drop of the suspension containing a suspension of nanoparticles is let to infiltrate the colloidal lattice. Since the nanocrystals are larger than the external pore size, only the liquid enters the lattice. (b) Then, the substrate is spun at high speed causing thinning of the coating layer and evaporation of the liquid. (c) Finally, a thin continuous layer of the guest compound is formed onto the lattice external surface.

Figure 6 shows the variation of the effective thickness of a nanocrystalline film deposited on the colloidal crystal, as estimated from the optical properties, versus the spinning speed of the substrate. The SEM images introduced as insets serve as examples of the different film shapes attained at the lower and the higher speeds employed. In this case, we employed a suspension of nanocrystalline titania in which different dispersants were present (size≈13 nm, Solaronix HT, suspension in a mixture of water, ethanol and polyethylene oxide). Basically, aggregates must be large enough as to prevent them from entering the opal like structure through the external pores and filling its interstitial space, but small enough as to allow the formation of a smooth coating of controllable thickness onto the colloidal lattice. Although the nanoparticle average size (l) is of the order of 10 nm, as measured by high resolution electron microscopy and in good agreement with X-ray diffraction measurements, the aggregation, which might be caused either by chemical bonding or flocculation, gives rise to a very different final average cluster size (⟨d⟩≈160 nm). On the other side, the colloidal crystal films employed in this work were formed by D=720 nm diameter polystyrene spheres. The size of the entrance windows,
\( w, \) is estimated as the diameter of the sphere that fits exactly between three spheres in the most external close packed (111) plane of the lattice, which corresponds to \( w=0.1547xD \) (in our case, \( w\approx110 \text{ nm} \)). SEM pictures in Figure 6 it can be seen that a smooth and highly uniform capping layer is achieved, allowing the subsequent formation of a good quality colloidal crystal onto it. These insets illustrate the typical shapes of films attained using speeds located at the two ends of the range under analysis. Control over the thickness of the defect slab is achieved by varying the spinning velocity. Deposited films are always in conformal contact with the bottom crystal, therefore presenting always corrugation in its lower face, as can be seen in the insets of Figure 6. Furthermore, for thin films this corrugation is also present in the upper side (see right inset in Figure 6). So, a rough estimate of the defect thickness (\( T \)) was extracted from the SEM images and a more precise one was attained from the fitting of the optical properties of the doped samples, discussed in detail later. Interestingly, thickness \( T \) versus spinning speed \( \omega \) data cannot be adequately fitted to a power law of the sort \( T\sim\omega^b \), which is the dependence observed for films made by spin coating reported up to date, being the empirical values of the exponent \( b \) typically around 0.5 for diluted polymers or glass precursors. Besides, in our case, the curve \( T \) vs. \( \omega \) shows an abrupt change in the thinning rate at around 80-100 rps. These anomalous effects may have their origin in the fact that our spin coating process is performed using a colloidal crystal as a substrate. First, the liquid phase of the crystallite suspension is removed not only by evaporation due to the fast spinning speed, but also it can be soaked by the porous substrate. The kinetics of this process may differ from that observed when a thin film is spun onto a dense wafer, deviations from the power law being possible. Second, unlike most spin coated films, our nc-TiO\(_2\) layer is deposited onto a periodically corrugated surface, which must also affect its spreading. In fact, the series of coatings made using \( \omega=100, 120 \) and 140 rps preserve the corrugation of the colloidal lattice surface. For thicker defect layers (i.e., lower spinning speeds), however, this inherited corrugation is greatly smoothed, as can be seen in the right inset in Figure 6. This change in the corrugation of the upper face of the deposited nanocrystalline film occurs at the same range of \( \omega \) for which the change in the thinning rate of the \( T \) vs. \( \omega \) curve is observed. The corrugation seems therefore to hinder the spreading of the nanoparticles in the forming film, resulting in a slower growth rate than that observed for thicker films.

![Figure 6](image-url) **Figure 6.** Observed dependence of the estimated thickness (\( T \)) of the deposited nanocrystalline titania layer with the spinning velocity (\( \omega \)). SEM images introduced as insets serve as examples of the different film shapes attained at the lower and the higher speeds employed.

The uniformity of the thickness of the deposited nc-TiO\(_2\) layer allows a new colloidal crystal to grow onto it by the vertical deposition method. Low magnification analysis of the cross sections of cleaved samples in the SEM, like that shown in Figures 7(a), confirmed that the quality of this upper lattice is similar to the lower one. Figure 7(b) shows a detail of the defect layer in which the different surface corrugation at both sides of the interface can be clearly observed.
The nanocrystalline defect layer behaves as an optical dopant causing the opening of well-defined allowed state bands within the forbidden frequency interval of the surrounding lattice. In our case, these are detected as narrow dips within the spectral range at which the (111) Bragg reflection is observed. Vertical dotted lines point out the position of such dips in the reflectance spectra. Curves in Figures 8(a)-8(c) correspond to differently doped samples, each one built using a different spinning velocity to deposit the defect layer. It should be noted that the dip induced by the presence of the defect at pseudogap frequencies presents a reflectance value close to that observed in the pass band region of the lattice, according to theoretical predictions. In the case of the defects herein presented, the nanocrystalline mid-layer is deposited without altering the composition of the lattice, hence maintaining its photonic strength.

![Figure 7](image_url)  
(a) Low and (b) high magnification SEM images of cross sections of a polystyrene sphere colloidal crystal containing a nanocrystalline titania defect layer deposited by spin coating.

![Figure 8](image_url)  
Figure 8. Specular reflectance spectra of polystyrene sphere colloidal crystals containing defect layers of different thickness. These layers were deposited using spinning speeds of (a) 120 rps, (b) 80 rps, and (c) 40 rps. The average diameter of the spheres the colloidal crystals are made of is 700 nm.

Changing the spin coater angular speed, since it controls the thickness of the defect layer, can be used to shift the defect state position at pseudogap frequencies. An example of the variation observed experimentally of the spectral position of the transmission window at pseudogap frequencies with the nc-TiO2 defect thickness is provided in Figure 8. Defect slabs of similar thickness may give rise to different intra-gap states depending on the width of the crystals surrounding it. For the case of thinner crystals, the Bragg peak broadens and therefore it is possible to attain planar cavity modes at frequencies outside the stop band limits of the infinite crystal.
5. CONCLUSIONS

In conclusion, we have proved that spin coating is a suitable technique both to infiltrate with a guest compound and to introduce a nanocrystalline planar defect within colloidal crystal films. This processing can be performed in minutes. A wide variety of compounds have been infiltrated, demonstrating the versatility and generality of the procedure. Defects are introduced without diminishing either the lattice quality or its photonic strength. Well-defined optical reflectance dips at pseudogap frequencies confirm the improvement with respect to previous techniques employed to dope this type of photonic crystals. We have also demonstrated that the spectral position of the defect states can be tuned through the size of the defect layer, which is controlled by the rotation speed of the substrate during the spin coating process. We foresee these optical materials might have applications in fields in which nanoparticulated materials are used as photochemically active compounds, such as photocatalysis or dye sensitized photovoltaics.

REFERENCES

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