

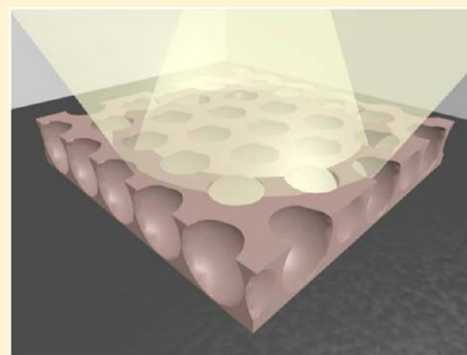
One-Step-Process Composite Colloidal Monolayers and Further Processing Aiming at Porous Membranes

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S Supporting Information

ABSTRACT: Composite materials consisting of a monolayer of polystyrene spheres (diameters of 430 and 520 nm) and porous silica, filling in the interstices, have been fabricated and characterized. The proposed growth method introduces some novelties as far as the fabrication of this kind of monolayers is concerned, as it probes the compatibility of coassembly (in which a silica precursor, tetraethyl orthosilicate (TEOS), is added to the base colloid) with confined growth in a wedge-shaped cell, while profiting from the advantages of both techniques. Using this method, it is possible to fabricate the composite monolayer in a single growth step. A systematic study of the influence of TEOS concentration in the initial colloid was performed in order to improve the quality of the two-dimensional crystals produced. Thus, it was demonstrated that the two methods are compatible. Furthermore, the composites were then subjected to thermal treatment so that the polymer is removed to reveal the inverse structure. After the calcination the membranes still present very good quality and so the proposed approach is effective for the fabrication of porous membranes. A comparison of reflectance spectra, between composite monolayers fabricated using this method and composites achieved by infiltrating polystyrene bare opals with silica chemical vapor deposition, is also established. The procedure presented is expected to establish the route for an easier and quicker fabrication of inverse monolayers of high refractive index materials with applications in light control.



1. INTRODUCTION

The pursuit of materials with uncommon optical properties has incredibly boosted the research effort in the photonics community. As far as the control of the radiation/matter interaction is concerned and, consequently, the manipulation of light, two-dimensional (2D) photonic crystals (PC) have proven to be strong candidates due to their versatility. Among those, slablike crystals based on the self-assembled arrangement of dielectric spheres are perhaps the most straightforward to obtain.¹ These systems can be implemented in applications such as filtering or waveguiding,² microlens arrays,³ and hybrid photonic–plasmonic materials.⁴ Additionally, they can play an extraordinary role as masks, in nanosphere lithography,⁵ or as templates for more complex colloidal structures;^{6–8} they are very effective for the production of nanoparticles⁹ and, from a fundamental point of view, they constitute an interesting subject of theoretical study.¹⁰

In order to accomplish this kind of 2D PC, self-assembly techniques are the simplest and most widely used. The most widespread one is probably the vertical deposition method,¹¹ starting from very dilute colloidal suspensions. This technique relies on convective particle assembly and delivers crystals consisting of dielectric spheres, arranged in a hexagonal lattice. Nonetheless, polycrystalline domain structure is a major limitation of the method. Consequently, a number of publications proposed refined processes of convective particle assembly and reported on the influence of different growth

parameters on the quality of the monolayers.^{12,13} It was recently shown¹⁴ that by controlling the geometry of the three-phase contact line, at the meniscus of the suspension, one can achieve better quality monolayers than those obtained by vertical deposition, in particular, single domain ones, centimeters across. The way to reach this is by confining the suspension in a wedge-shaped cell. The particularity of this kind of evaporation cell is that it permits an almost rectilinear interface between the three phases involved during the evaporation.

Despite the considerable interest that these 2D arrangements of spheres can raise, there is also a significant demand on the fabrication of the inverse structures, that is, membranes composed of nanobowls or nanopore arrays or interconnected air voids.¹⁵ Inverse structures, based on colloidal crystal monolayers, might be used for the development of gas sensors¹⁶ and superhydrophobic surfaces,¹⁷ evaporation masks,¹⁸ templates for cell growth,¹⁹ or protein self-assembly;²⁰ for the study of photoluminescence;²¹ or even for the enhancement of magnetic properties of thin films.²² They have been produced with diverse compositions such as inorganic materials,¹⁷ oxides,^{23,24} semiconductors,²⁵ metals,²⁶ or polymers.^{27,28} With regard to fabrication, the inverse

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monolayers have been achieved by infiltration with techniques such as electron beam evaporation,²⁹ doctor blade technique,³⁰ solution/sol-dipping, or electrodeposition.³¹ Additionally, gas phase deposition techniques can also be used for the infiltration, with additional advantages. They permit a very good degree of conformality of the deposited material and also fine-tuning of the film thickness.³²

On the other hand, with respect to 3D crystals, recent experiments pointed out that good-quality, crack-free, inverse opals could be fabricated in a two-step method using coassembly.³³ The obtained crystals presented a high degree of order, over length scales of centimeters. The mainstream method to produce inverse opals is essentially (a) growth of a bare opal of sacrificial material, (b) infiltration with the desired material, and (c) selective removal of the sacrificial material. Using coassembly, the composite is obtained in a single step in which a chemical precursor of the background material is added to the spheres' suspension. Therefore, it grows in the spheres' interstices at the same time that the spheres assemble. Subsequently, using calcination or plasma etching, the sacrificial spheres are removed and the inverse opal is obtained. Moreover, the authors show that direct conversion into other materials (silicon and titania) is possible using shape-preserving gas/solid displacement reactions.

In this work, we test the possibility of fabricating silicon oxide inverse monolayers using a sol–gel approach and combining the wedge-shaped cell growth, on the one hand, with coassembly on the other. By adopting this procedure, it is hoped that one might benefit from the advantages that both techniques permit. In comparison with similar tests, previously carried out by other groups, our approach has the advantage of achieving the composite (polystyrene spheres embedded in silica matrix) in one single step, as opposed to the work of Li et al.,³⁴ which relies on sol-dipping, and also of increasing the effective macroscopic area of the final monolayers; Lu et al.³⁵ reported a typical ordered area of $100\ \mu\text{m}^2$, while we were able to obtain monodomain areas around $1000\ \mu\text{m}^2$. Furthermore, we compare the obtained crystals with similar ones produced by infiltration of bare monolayers with chemical vapor deposition (CVD).

2. EXPERIMENTAL SECTION

The polystyrene (PS) spheres used in this work were commercially acquired (Thermo Scientific). Two diameters were compared, 430 and 520 nm, with polydispersity below 3%. The samples fabricated by CVD infiltration were first grown by the usual vertical deposition method and then infiltrated in a homemade CVD line. The silica precursor used was silicon tetrachloride (SiCl_4). Further details on CVD infiltration can be found elsewhere.³² The second kind of monolayer was grown on glass substrates using the wedge shaped cell method. More details are provided in ref 12. Briefly, the substrates were carefully cleaned in a detergent and water ultrasound bath. Then, they were rinsed with distilled water, dried under a nitrogen flux, and immersed in a hydrogen peroxide solution at $80\ ^\circ\text{C}$, for approximately 1 h. Afterward, they were rinsed and dried once again. Finally, the wedge-shaped cells were assembled accordingly to the Scheme S1 provided in the Supporting Information. The angle described between the substrate and the cover slide was 2° .

The concentration of spheres was kept constant in all the suspensions ($100\ \mu\text{L}$ of the commercial suspensions at 10 wt %, which totals a final concentration of 0.5 wt %). The silica precursor used was a mixture of ethanol, 0.1 M HCl in water, and tetraethyl orthosilicate (TEOS) in the mass ratios of 1.5:1:1, stirred for 1 h; for convenience this mixture is called TEOS throughout the text. Sets of crystals were fabricated varying the added volume of TEOS to the

initial colloid from 20 to $120\ \mu\text{L}$. This corresponds to a concentration range from 1 to 6 vol %. The total volume of the suspensions prepared was 2 mL for all cases. The suspensions were prepared in clean glass vials. First, the distilled water ($18.2\ \text{M}\Omega$) was poured into them, then the respective volume of precursor was added, and last the spheres. In order to homogenize them, the vials were briefly immersed in an ultrasound bath. Finally, a volume of $100\ \mu\text{L}$ of the suspension was inserted into the wedge cell with the aid of a micropipet. Afterward, the cells were placed in a climatic chamber, over a polymeric platform in order to minimize vibration. The chosen temperature was $20\ ^\circ\text{C}$ and relative humidity 90%. Typically, four samples were repeated for each concentration in order to minimize the intrinsic variability of the fabrication process. The samples are withdrawn after approximately 24 h.

At a later stage, the samples were treated in order to remove the polymer of the composite and obtain the inverse matrix. They were subjected to calcination in a tubular furnace. First, the temperature was raised from room temperature to $90\ ^\circ\text{C}$ at a rate of $1\ ^\circ\text{C}/\text{min}$. This ramp was followed by a plateau of 3 hours at $90\ ^\circ\text{C}$. Afterward, the sample was heated until a temperature of $450\ ^\circ\text{C}$ was reached, at a rate of $1\ ^\circ\text{C}/\text{min}$. The monolayers were maintained at this temperature for 8 h. Finally, the cooling was performed at $5\ ^\circ\text{C}/\text{min}$ until the temperature of $30\ ^\circ\text{C}$ was reached.

Their structural characterization was accomplished with a FEI NovaNano SEM 230 microscope. In the analysis of SEM images, it is assumed that the infiltration of silica is complete and occupies all the volume available in the spheres' interstices, from $z = 0$ (which corresponds to the location of the glass substrate) to $z = h$, which is the maximum thickness of the silica film, as was explained previously. The expressions for the height h and the filling fraction f presented at a later time can be straightforwardly derived from geometric considerations.

The normal incidence reflectance spectra were collected with a FTIR Bruker IFS 66/S spectrometer coupled to a microscope, which permits a good selection of the test area. The Fourier image optical characterization was carried out in a homemade setup.

3. RESULTS AND DISCUSSION

In this section, the samples obtained by the two different techniques mentioned above are compared. In the first case, the characterization of the crystals composed of PS spheres, infiltrated with silica using CVD, is introduced while the following section refers, instead, to the analogous system, fabricated with coassembly in the confinement cell. A statistical analysis of the quality of the composites is presented herein. In the final section, the corresponding data relative to the inversion of the systems is shown.

3.1. PS Spheres in Silica Matrix by CVD. Normal incidence reflectance spectra of a PS monolayer infiltrated with silica using CVD are shown in Figure 1. Each curve corresponds to an incremental number of CVD cycles. In the figure, the frequency is displayed in terms of relative units ($\sqrt{3\varphi/2\lambda}$) where φ is the diameter of the spheres and λ the wavelength of the electromagnetic radiation in a vacuum. The spectrum measured for the bare crystal shows a broad interference dip in the low-frequency region, centered at 0.52 and some slighter dips centered at 0.84, 0.93, and 1.04. They can be interpreted as Fabry–Perot resonances, considering the crystal as a uniform dielectric slab.³⁶ Near $\sqrt{3\varphi/2\lambda} = 0.68$ a much narrower dip is observed that is assigned to the onset of diffraction by the periodic lattice. This dip is also known as the Rayleigh–Wood anomaly.

Infiltrating with silica, which possesses a refraction index similar to that of PS, one induces a decrease of the index contrast of the system, and this leads to the attenuation of the scattering strength, since lateral modulation is neutralized.

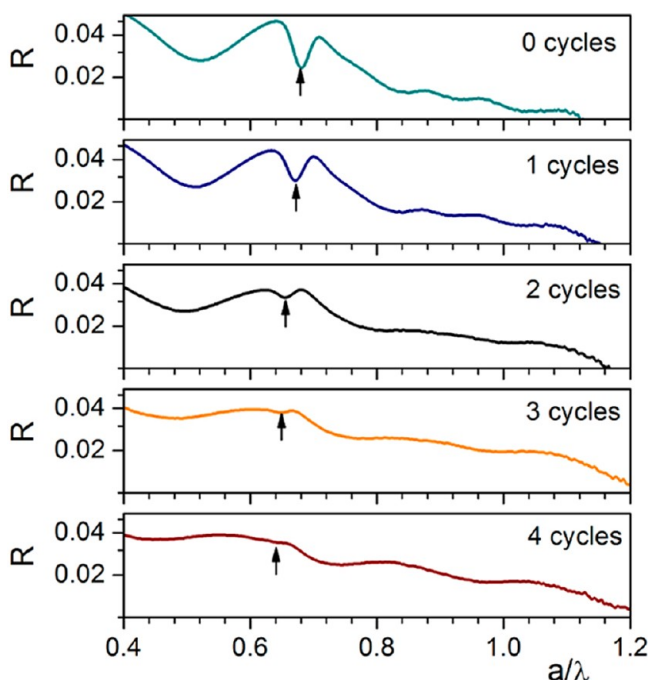


Figure 1. Reflectance spectra of a monolayer of PS spheres as a function of CVD cycles of silica infiltration. The horizontal axis is presented in relative units ($\sqrt{3}\phi/2\lambda$). The arrow highlights the spectral position of the Wood's anomaly, which becomes attenuated as the refraction index contrast decreases.

Additionally, one observes a red shift of the mode, which is in accord with the increase of the effective dielectric constant of the medium, as silica progressively substitutes for air in the composite.

We propose a different approach that aims at the fabrication of an inverse silica monolayer, using a two-step method. This fabrication scheme permits the straightforward achievement of an opened topology which to be obtained by CVD infiltration would require an additional etching step. This is a drawback, as expensive techniques like reactive ion etching are required to carry out etching of the top surface. In what follows, the systematic analysis of the composite is reported and then the inverse monolayer is presented.

3.2. PS Spheres in Silica Matrix by Wedge-Shaped Cell and Coassembly. The details of fabrication of the samples consisting of PS spheres in the silica background fabricated with the wedge-shaped cell method and by coassembly are provided above, in the Experimental Section. A common feature is observed in all the monolayers grown. They typically exhibit three different regimes of growth, as can be appreciated in Figure 2, which shows examples of optical microscopy photographs. The first regime (Figure 2a) occurs mainly at the beginning of the process, but sometimes it also extends along the growth direction (especially near the borders of the confinement cell). In this regime the samples present poor quality, with disorder, small domains, and even the formation of multilayers. After some elapsed time, the growth stabilizes and a good-quality composite monolayer starts to develop; this is the second regime, depicted in Figure 2b. In this region (as in the previous one), the infiltration with silica takes place. At some point, the condensation reaction is terminated and bare monolayer grows from there on; this is the third regime, as observed in Figure 2d. A marked frontier separating the last two

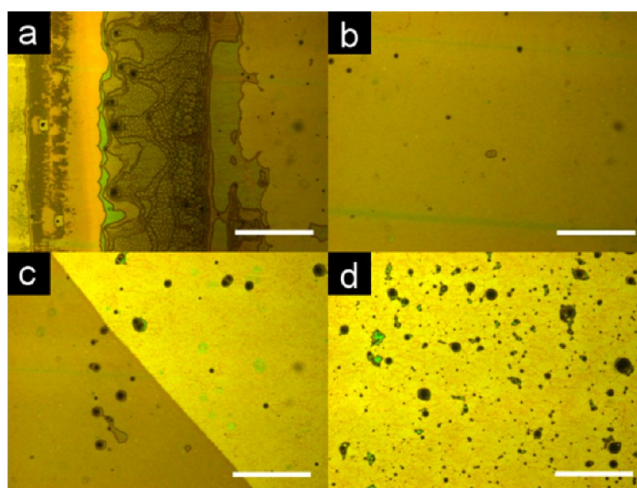


Figure 2. Three growth regimes can be identified by observing the samples at the optical microscope: beginning of the growth exhibiting poor quality (a), silica infiltrated monolayer (b), and bare monolayer (d). The transition between the two last regions is abrupt (c). In this example is shown the sample grown with spheres of diameter $\phi = 430$ nm and $[\text{TEOS}] = 1.5$ vol %. The scale bar corresponds to $250 \mu\text{m}$ in all cases.

regions is observed (Figure 2c). From the comparison of parts b and c Figure 2, it is seen that the amount of defects that appear in the bare region, typically as small islands of two or three layers, is larger than in the composite region. The defects are identified as darker spots standing out from the bright background. That observation is also a general feature of the samples studied.

To the naked eye, the crystals grown with spheres of diameter $\phi = 430$ nm start to nucleate nearer the borders of the substrate. In fact, for almost all the samples a V shape is observed. As the growth proceeds, those regions expand toward the center, and at some point they meet. After this, the material grows as a continuous region occupying all the substrate's width. Near the borders the samples exhibit intense colors and iridescence while the center region usually presents a milkier aspect that is characteristic of a disordered material. On the other hand, very good quality and large regions were obtained for the samples grown with spheres of $\phi = 520$ nm. In these, the three regimes mentioned above were also observed, but to the naked eye, the crystal develops along all the width of the substrate, right from the beginning. As expected, the infiltrated areas are slightly more transparent due to the lower refraction index contrast and thus to the lower scattering efficiency.

A quantitative analysis of the above-mentioned aspects is summarized in the Figure 3. The data points were collected by hand-drawing the contours of the regions of interest, digitalizing the contours, and then using software to calculate their respective area. The analysis showed that the percentage of good-quality infiltrated area of the sample with respect to the total initial area covered by the colloid ($2.6 \times 1.5 \text{ cm}^2$) is on the order of 15% in the case of the samples grown with $\phi = 430$ nm spheres. In this case, low precursor concentrations favor the extension of the infiltration. In the case of the samples grown with spheres of $\phi = 520$ nm, the best result was obtained for $[\text{TEOS}] = 2.0$ vol % with an infiltrated area on the order of 25%. In general, for most TEOS concentrations studied, these samples performed better than their low sphere diameter counterparts, except for $[\text{TEOS}]$ above 5.0 vol %. Possibly, the

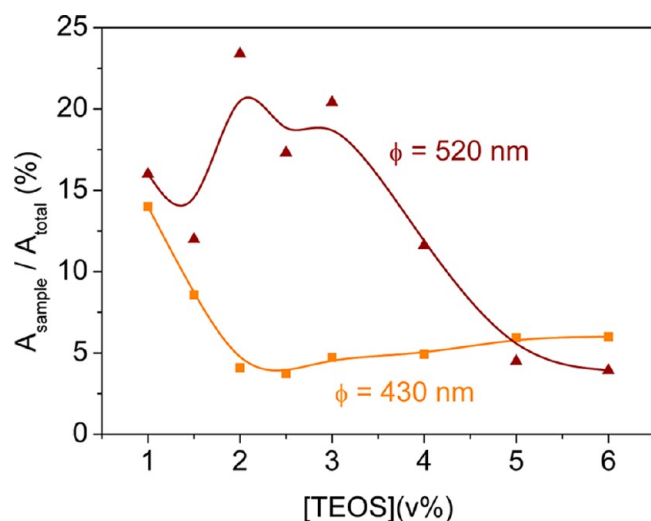


Figure 3. Quantitative analysis of the good-quality infiltrated area (A_{sample}) with respect to the total area, susceptible of growing (A_{total}), versus concentration of TEOS. A_{total} is the area initially occupied by the liquid colloid. The lines are simply a guide to the eyes. Squares (triangles) express results for samples grown with spheres of diameter 430 (520) nm.

parameters that might induce these significant differences are the angle described by the wedge-cell and the type of spheres or surfactant present in the commercial suspension. In fact, some preliminary experiments have shown that the angle of the cell should be slightly tuned according to the diameter of spheres used. Nevertheless, a study of the quality of the samples as a function of the referred angle was out of the scope of the present work. Regarding the type of stabilizers of the commercial suspensions, it is possible that they have an effect on the colloid. This could not be ascertained, as details about the commercial colloids are proprietary information.

SEM analysis permitted one to corroborate that the differences between the two kinds of regions observed in each sample are due to the presence or absence of silica. It showed that the areas corresponding to the mentioned second regime were formed of composite material, while the areas corresponding to the third regime were not infiltrated. Figure 4 shows several examples of SEM photos of samples fabricated with spheres of 430 nm diameter. The concentration of SiO_2 precursor used for the sample shown in parts a and b was 1.0 vol %, while it was 2.5 and 4.0 vol % in the sample of parts c and d of Figure 4, respectively. In all cases, one can observe a good degree of order and extensive monodomain regions, which is illustrative of the order found in the typical grown crystals. In Figure 4a, part of a much larger monodomain (Figure S1 of Supporting Information) of approximately $8500 \mu\text{m}^2$ is exhibited. The good quality of the samples is perturbed by some defects as spheres detach from the matrix at some points, originating cracks like those shown in Figure 4d, possibly during the drying process. Frequently, point defects such as missing spheres or slightly different diameter spheres and linear defects like dislocations are observed. Nevertheless, the overall extension of monodomains is typically preserved. This degree of quality was also found for the samples grown with $\phi = 520$ nm spheres.

Microscopy showed that the single domains are typically very broad, of the order of $1000 \mu\text{m}^2$. Nevertheless, perfect regions do not present such large areas. These were defined as smaller

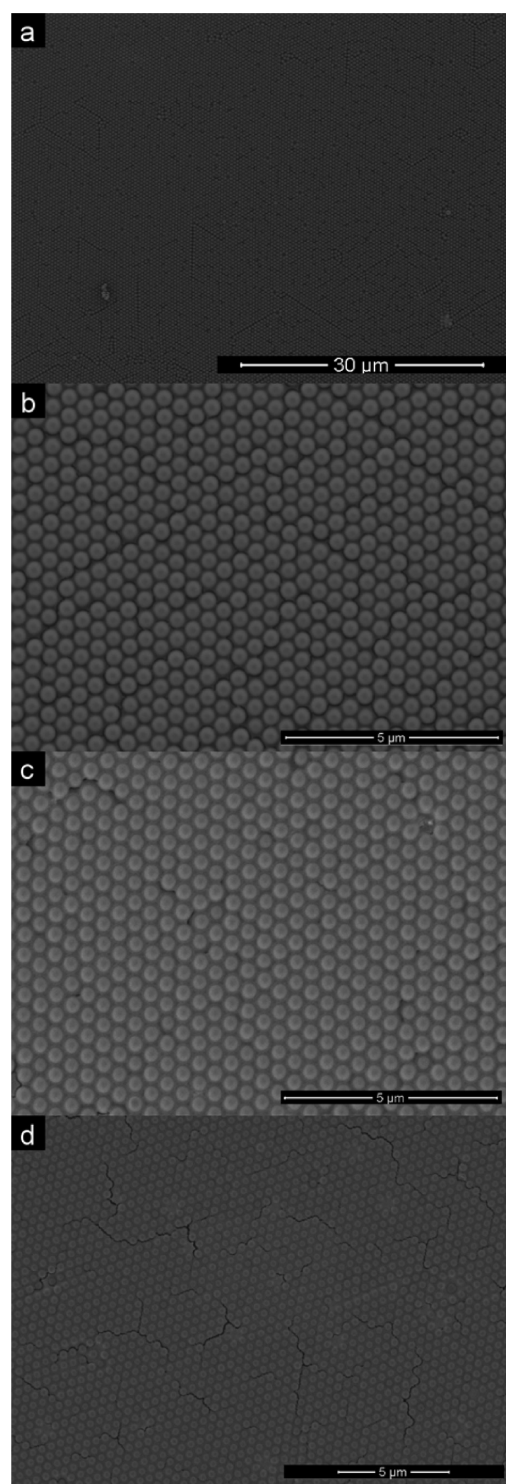


Figure 4. SEM images of samples fabricated with spheres of $\phi = 430$ nm, [TEOS] = (a and b) 1.0 vol %, (c) 2.5 vol %, and (d) 4.0 vol %. Notice the very large domains and that the concentration of the silica precursor induces slight changes in the degree of infiltration.

parts of the crystals which belong to the same monodomain, although they present cracks originated in the drying phase, as is exemplified in Figure 4d. Figure 5a shows a statistical analysis of the average area of these smaller crystallites. The areas were estimated with the help of drawing software, and averages were taken from typically 10 regions belonging to various images. Despite data dispersion, a clear quality improvement was

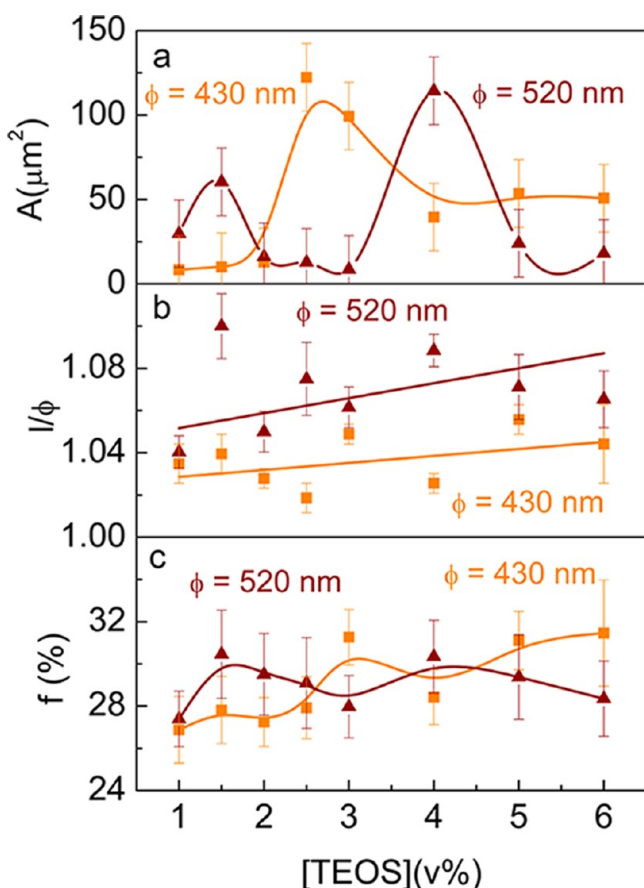


Figure 5. The average area of good-quality, crack-free areas, inside the larger monodomains of the composite monolayers (a), normalized lattice parameter (b), and filling fraction (c) for different TEOS concentrations. For better comparison, the lattice parameter (l) was normalized with respect to the sphere's diameter. With the apparent diameter and the lattice parameter one can extract the filling fraction of the silica (f). Squares (triangles) express the results for samples grown with spheres of diameter 430 (520) nm. The drawn curves simply intend to highlight the general tendency of the data and do not correspond to any theoretical fitting.

observed for determined [TEOS]. Maxima are observed in both curves corresponding to the two diameters studied. In both cases, the best areas of crystallites reached were on the order of 120 μm^2 . The maximum area was obtained for [TEOS] = 2.5 vol % in the case of the 430 nm samples, while in the case of the samples produced with larger spheres, the maximum was observed for the crystal fabricated with [TEOS] = 4.0 vol %. The fact that there is an optimal TEOS concentration is not surprising, because if it is too low it is not possible to reach a continuous silica film, filling in the interstices between spheres, and if it is too high, the quantity of additional charge introduced in the colloid is significant and this induces rheological instability.

The most remarkable aspect resulting from the analysis of the SEM images is the fact that the apparent diameter of the spheres (ϕ_{app}), which corresponds to their diameter observed in surface view, presents a tendency to decrease, as the added quantity of TEOS in the starting suspension increases. Assuming a complete infiltration, the decrease in ϕ_{app} implies that the infiltration height, h , defined as

$$h = \left(\frac{\phi}{2}\right) + \sqrt{\left(\frac{\phi}{2}\right)^2 - \left(\frac{\phi_{\text{app}}}{2}\right)^2} \quad (1)$$

increases. This fact suggests that it is possible to change the filling fraction (f) of the silica in the final inverse matrix by acting on the concentration of its precursor. The filling fraction is defined as

$$\frac{f}{100} = \frac{h}{\phi} - \frac{\pi h^2}{3\sqrt{3}l^2\phi}(3\phi - 2h) \quad (2)$$

This phenomenon is in accord with previous observations in similar systems, for which it was reported that it is possible to control the morphology of the grown inverse monolayer by controlling the concentration of the infiltrating precursor.²³ In order to carry this analysis further and ascertain the behavior of f , it is also necessary to account for the lattice parameter (l), which is defined as the distance between spheres. In all samples, due to the presence of silica, it was verified that l is larger than the sphere's diameter, which implies that the material organizes in cermet topology. On the contrary, in regions belonging to the third regime of growth, apart from intrinsic defects, the structure assumes a close-packed form.

A systematic analysis of the apparent diameter of the spheres in the composite, the lattice parameter, and filling fraction was carried out. The results for the latter two are summarized in the Figure 5b,c. Concerning the samples produced with spheres of $\phi = 430$ nm, a linear fit of the experimental data showed that the normalized lattice parameter increases approximately 2%, accompanying the increase of [TEOS] from 1 to 6 vol %. In the same range, the increase of the filling fraction is on the order of 5%. For the samples with spheres of $\phi = 520$ nm, the increase in l is on the order of 4%; nevertheless, the change in f is less significant: only an increase of 1% was observed. Although the mentioned linear fits exhibit the expected behavior, it is necessary to point out that, for both sets of samples, a monotonic increase of the filling fraction is not evident. Care should be taken as the observed change in f is on the order of the experimental error. The error was estimated by applying the propagation equation to f and assuming the standard deviation as the error of ϕ_{app} and l . Although the data are noisy, it suggests that for low concentrations of the precursor, the degree of infiltration is higher in the samples fabricated with spheres of $\phi = 520$ nm. As the concentration of TEOS increases, this relation is inverted and the filling fraction becomes higher for the samples with $\phi = 430$ nm. The inversion occurred approximately for [TEOS] = 3.0 vol %.

In order to further detail the characterization of the crystals, Fourier image spectroscopy was employed in reflectance mode. This is a very powerful technique, as it permits the angle-resolved collection of the spectra and thus the direct probing of the dispersion relation. Although differences in the filling fraction of the composite could not be resolved for different concentrations of TEOS, the second and third regime of growth were compared and analyzed in the framework of an effective medium model. The results are presented as gray scale plots in Figure 6. The figure shows an example for the case of the monolayers produced with spheres of $\phi = 520$ nm.

Results are presented for increasing angles of incidence along the two high-symmetry directions in reciprocal space for a hexagonal lattice: ΓM and ΓK . In the plots corresponding to the experimental results of the bare crystal, a number of modes appear as lines crossing at $\lambda \sim 650$ nm at the Γ point. The

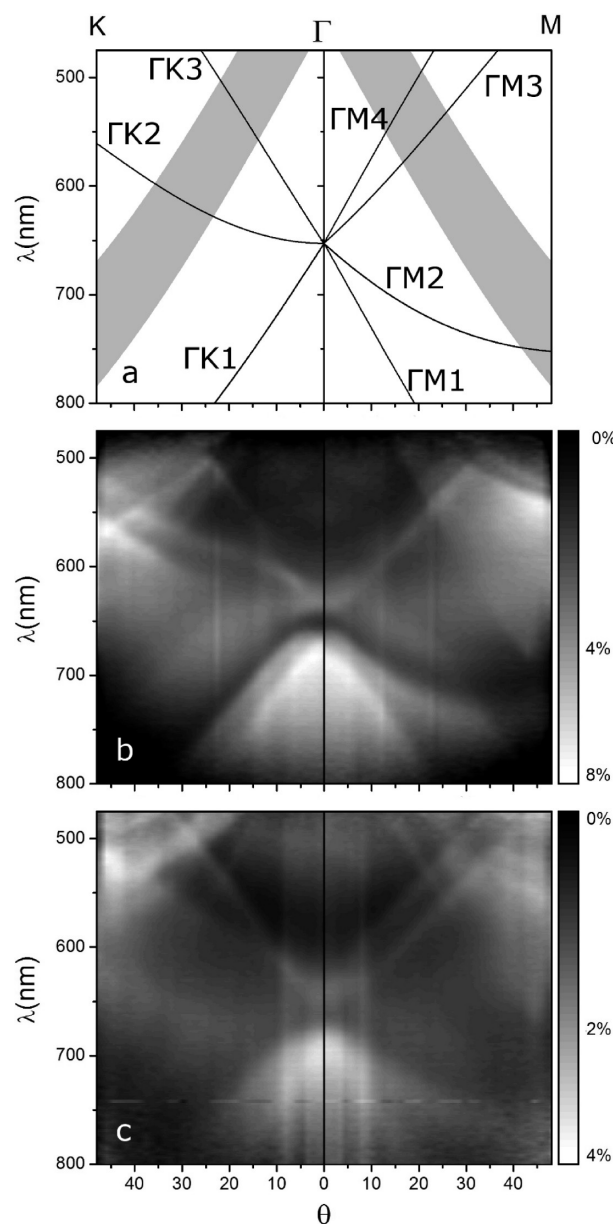


Figure 6. Theoretical dispersion relation of a direct monolayer of PS spheres (a). Parts b and c present the experimental angle-resolved reflectance resulting from Fourier image spectroscopy of a bare monolayer and composite, respectively.

dispersion of the different modes is clearly different for the two directions considered. In order to account for these results, we have employed an effective medium model.³⁷ In this approach, one considers a medium having a real refractive index n_{eff} with a linear dispersion relation. The effect of the periodicity is introduced in two ways: folding the dispersion relation at the Brillouin zone edges (bands ΓM1 , ΓM4) and taking into account the diffraction by different reciprocal lattice vectors (bands ΓM2 , ΓM3 , $\Gamma\text{K1-3}$). The outcome of this model assuming an $n_{\text{eff}} = 1.45$ is shown in Figure 6a. Here it is evident that the overall shape of the experimental dispersion relations is well-reproduced.

In order to get a good agreement between the theoretical bands and the experimental ones, a much higher effective refractive index had to be assumed than that expected from the effective medium approximation—1.45 versus 1.35—that

would result from the weighted volume average of the two indices composing the monolayer, considering a filling fraction of PS of 60% and 40% of air. This can be explained by examining the spatial distribution of the total field intensity. The contributing modes correspond to guided modes of the monolayer, so it is shown that in the system under study, the total field intensity becomes much more concentrated inside the spheres. For this reason, the actual refractive index the radiation feels is higher.³⁷

The broad gray bands in Figure 6a represent the first-order diffraction onset and the re-entrance in the detector.³⁷ They can also be observed in the measured spectra, and the positions are in good agreement. Furthermore, this agreement is also verified in the case of the modes ΓK1 , ΓK3 , ΓM1 , ΓM2 , and ΓM3 . The position of the ΓK2 mode is also well-predicted. In the collected spectra it is possible to observe another mode adjacent to it. Actually, it is verified that the ΓK2 branch corresponds to two modes whose degeneracy is lifted, as can be seen in the experimental measurement. Finally, concerning the ΓM4 mode, it is the least intense, as expected, but its slope, in the dispersion relation, is higher than expected.

The spectra of the composite were also measured and are presented in the Figure 6c. The results are exemplified for the case of the sample fabricated with $[\text{TEOS}] = 1.0$ vol %. We note that the signal-to-noise ratio is less and that the reflectance of the sample drops to approximately half that in the previous case. This is due to the decrease in the contrast between the refractive indices forming the lattice. Two important changes take place when comparing the gray scale plots of the bare monolayer with those from the composite. The first concerns the spectral position of the origin of the modes, in the Γ point. In the case of the direct structure, it is found at $\lambda = 646$ nm, while for the composite it displaces to lower energy ($\lambda = 657$ nm). The second one is the observation of a slight decrease of the slope of the modes in the dispersion relation. This is especially visible in modes ΓK3 , ΓM3 , and ΓM4 . Both changes are consistent with the increase of the effective refractive index and lattice parameter induced by the presence of the silica, which was also verified by the SEM analysis.

The spectra introduced in Figure 1 would correspond to a vertical section of the plots of Figure 6, with $\theta = 0^\circ$. The spectral range scanned in the latter ones corresponds in reduced frequency to the interval $[0.56; 0.95]$. The net red-shift and the decrease in intensity observed in the above gray scale plots (particularly for the Rayleigh–Wood anomaly), for the samples fabricated by coassembly is consistent with the results previously presented for the samples fabricated with CVD infiltration. Therefore, we demonstrate the effectiveness of the proposed fabrication method for the achievement of composites made of PS spheres in a silica matrix. It is necessary though to bear in mind one important difference. The morphology of the two kinds of samples is distinct; in particular, the surface pores of the monolayers produced by coassembly are open, while in the case of the CVD silica infiltrated crystals they are closed. If the specific application for the crystal requires open pores, an additional etching step of the surface would be necessary, in the second case.

3.3. Air Voids in Silica Matrix. The second step of the fabrication of the inverse monolayers consisted of the removal of the sacrificial PS spheres. For this, calcination and plasma etching were tested. It was verified that the calcination leads to similar results as the oxygen plasma etching, and that being so, both processes introduce some amount of defects and cracks in

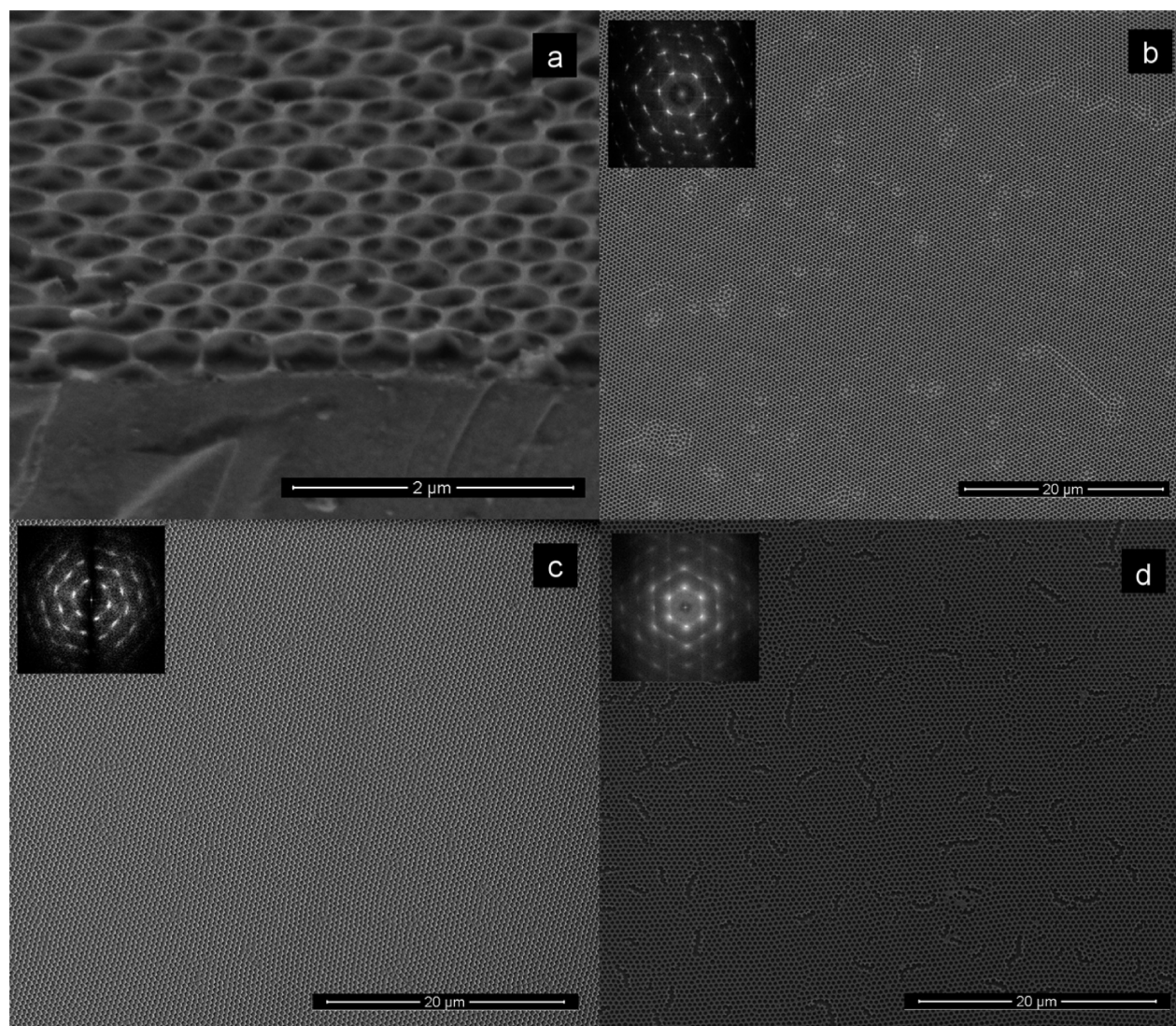


Figure 7. An example of a high-magnification SEM image of the inverse monolayer, in cross section (a) with $[\text{TEOS}] = 2.0$ vol %. SEM images at low magnification of samples grown with $[\text{TEOS}] =$ (b) 1.0 vol %, (c) 2.0 vol %, and (d) 3.0 vol %. Samples fabricated with spheres of 430 nm diameter. It is possible to appreciate good quality and wide domains after the thermal treatment. The insets of parts b, c, and d show the digital Fourier transform of the respective image.

the matrix. Therefore, calcination was the adopted treatment. Further details are explained in the Experimental Section.

Figure 7 shows the aspect the monolayers present after calcination. These SEM images are examples of the samples fabricated with spheres of 430 nm of diameter and $[\text{TEOS}] = 1.0, 2.0$, and 3.0 vol %. The images taken in cross section, as exemplified in Figure 7a, confirm that the 3D structure is preserved as expected and that the infiltration surpasses the equator of the spheres. The thickness h of the monolayer can be estimated by measuring the thickness observed in the image and correcting it with the tilt angle. In this example, the thickness obtained is 260 nm. From the low-magnification images, such as the ones presented in Figure 7b–d, the hexagonal pattern is visible and large monodomain regions are preserved. The area of the exhibited monodomain in Figure 7b is approximately $2900 \mu\text{m}^2$, the one of Figure 7c is $2100 \mu\text{m}^2$ and the one from Figure 7d is $2000 \mu\text{m}^2$. While in Figure 7b some point defects are observable which originate in the formation of the composite, due to missing spheres or different size spheres, in Figure 7c all region presents minimum defects.

In Figure 7d cracks can be observed that are associated with the drying step and posterior thermal treatment. It is probable that for high $[\text{TEOS}]$ the grown silica is less porous, which gives rise to increasing mechanical tension during the removal of the spheres, and small cracks like the ones exhibited in Figure 4d increase in size. The insets of parts b–d of Figure 7 show the digital Fourier transform of the images and permit one to appreciate the 6-fold symmetry characteristic of the lattice, as individual points in the reciprocal space. This is strong evidence of the good quality of the monolayers, even after calcination.

Fourier image spectroscopy was also used in this case, although it was not possible to infer any characteristic optical features from the collected contour plots. This was due to the fact that the reflectance signal is too low. This was expected, as the inverse monolayer has a small amount of matter and hence a negligible scattering strength. In theory, according to eq 2, the maximum silica volume fraction in a closed packed structure is 40%. In the case of our system, the filling fraction is at most on the order of 30%, which implies, in the context of an effective

medium theory, that the net refractive index is only ≈ 1.1 as opposed to that of the composite (≈ 1.6).

4. CONCLUSIONS

The optimal growth parameters for the fabrication of composite monolayers consisting of ordered arrays of PS spheres in a silica background were searched in order to achieve the widest areas of infiltration, as well as to achieve the best quality at the microscopic level. We studied the correlation between the concentration of the silica precursor in the original suspension with the degree of infiltration of the sample and the thickness of the silica layer. Although linear fits of the filling fraction as a function of [TEOS] exhibit a slight increase for samples produced with spheres of 430 and 520 nm of diameter, a definite tendency is not advanced as the experimentally found values do not stand out significantly from the experimental error.

Angle-resolved reflectance spectra permitted to access optical properties of the monolayers and to demonstrate equivalence between the samples produced by coassembly and by CVD infiltrated bare ones. At a later phase it was shown that the composite structure is robust enough to withstand the thermal treatments used for the removal of the PS spheres. Thus, although defects are introduced by the calcination, it is possible to obtain large area inverse monolayers of good quality.

The reported results are interesting, as they demonstrate that coassembly growth is compatible with the wedge-shape confinement method, for the fabrication of composite monolayers. Thus, it is possible to reduce the number of steps to produce these structures while taking advantage of the increased quality attainable by the cell confinement. Moreover, this material serves as basis for the inverse monolayer, achieved by thermal treatment.

The procedure here presented allows for versatile control over the composite morphology and thus its optical response. Though the current approach is based on the use of SiO_2 , the applicability of the method is currently being studied for higher refractive index materials such as TiO_2 ³³ or silicon.³⁸ Their use could grant higher light–matter interaction. Further, the possibility of adding metallic components could pave the way to realize hybrid photonic–plasmonic systems whose optical properties are being actively explored.^{39,40} We hope that the kind of system proposed here might be applied in solar cells or sensing. Moreover, silicon porous membranes, for example, are expected to be useful as anode materials in rechargeable Li ion batteries.⁴¹ Optionally, the proposed growth can be applied in surface patterning or in the production of nanostructured templates.

■ ASSOCIATED CONTENT

Supporting Information

A scheme of the wedge-shaped cell and a SEM image showing an example of a large monodomain of the composite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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