Surface nano-structuration using composite colloidal monolayers

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Two dimensional (2D) photonic crystals (PC) have proven to be strong candidates for the control of the radiation/matter interaction and are a successful example of the research investment made by the photonics community. Furthermore, slab-like crystals based on the self-assembled arrangement of dielectric spheres are perhaps the most straightforward to fabricate [1]. These systems can be implemented in applications such as filters, waveguides and hybrid photonic-plasmonic devices. They can play an extraordinary role as masks, in nanosphere lithography or as templates for more complex colloidal structures and are also very effective for the production of nanoparticles.

The self-assembly methods are the simplest way to produce this kind of 2D PC, the most widespread being probably the vertical deposition starting from very dilute colloidal suspensions. Relying on convective particle assembly, this technique delivers crystals consisting of dielectric spheres, arranged in a hexagonal lattice. One of its important drawbacks is, nonetheless, polycrystalline domain structure. As so, the constant effort for improving the quality of the crystals resulted in several publications proposing alternative approaches for their fabrication, as well as reporting on the influence of different growth parameters.

A recent work [2] has shown that 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.

Furthermore, 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 [3]. Inverse structures are useful, for example, for the development of superhydrophobic surfaces, evaporation masks and templates for cell growth or protein self-assembly. Additionally, they are suitable systems for the study of photoluminescence manipulation [4]. Regarding fabrication, the inverse monolayers have been achieved mainly by infiltration with techniques such as electron beam evaporation, solution/sol-dipping, doctor blade technique or electrodeposition. Gas phase deposition can also be used for the infiltration, with additional advantages particularly, very good degree of conformality of the deposited material and fine tuning of the film thickness [5].

On the other hand, with respect to 3D PC, recent experiments pointed out that good quality, crack-free, inverse opals could be fabricated in a two-step method using co-assembly [6]. With this method, the composite (polymeric spheres immersed in a silica matrix) is obtained in a single step by adding a chemical precursor of the background material to the spheres' suspension. Therefore, the silica grows in the spheres' interstices, at the same time that the spheres assemble. Subsequently, the sacrificial spheres are removed using calcination or plasma etching and the inverse opal obtained.

In the work here presented, we tested the possibility of fabricating composite monolayers by combining the wedge shaped cell growth, on the one hand, with co-assembly on the other. By adopting this procedure, it was hoped that one might profit from the advantages that both techniques permit. Further thermal processing of the crystals permits one to attain the inverse porous membranes.

As so, composites were fabricated starting from colloidal suspensions of submicron spheres (diameters of 430 or 520 nm) in distilled water and added tetraethyl orthosilicate (TEOS) – the silica's

precursor. The suspensions are introduced in wedge shaped cells and left to evaporation in a climatic chamber with controlled temperature and humidity. A systematic study of the influence of TEOS concentration in the initial colloid (ranging from 1.0 to 6.0 vol%) was performed in order to improve the quality of the 2D crystals produced. The samples were characterized with scanning electron microscopy in order to ascertain the area of the perfect quality regions and filling fraction of the infiltrated silica. Figure 1 presents an example of a SEM image showing the surface of one of these monolayers. Furthermore, reflectance spectra of the obtained crystals were compared with the ones of similar crystals produced by infiltration of bare monolayers with chemical vapor deposition (CVD).

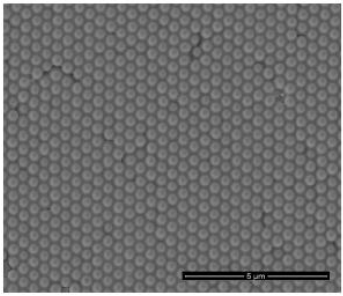

Figure 1: Example of SEM image exhibiting the surface aspect of the composite materials made of polystyrene spheres in a silica background.

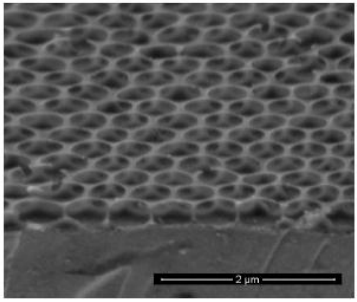

Figure 2: Example of SEM image, collected in cross section, exhibiting the aspect of the monolayers after calcination.

The effectiveness of the proposed fabrication method for the production of the composites was demonstrated. In a second phase of the work, the monolayers were calcinated in order to remove the polymer and achieve the inverse structure composed only of silica. An example of the crystals obtained with the referred procedure is shown in Figure 2. The results point out that the structures are robust enough to withstand the thermal treatments used in the inversion and, although defects are introduced, it is possible to obtain large area inverse monolayers of good quality.

The work described has been recently accepted for publication [7]. In comparison with similar experiments, previously carried out by other groups, our approach has the advantage of achieving the composite in one single step and also of improving the effective area of the final monolayers. We were able to obtain monodomain areas of the order of 1000 μm^2 with maximum perfect crack-free regions of approximately 120 μm^2. The procedure presented is expected to establish the route for an easier and quicker fabrication of inverse monolayers of higher refractive index materials, particularly silicon [8], with applications in light control.

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