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Review

Colloidal crystals as photonic crystals

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Abstract

Colloidal crystals (CC) are closely related to photonic crystals (PC) as both of them can be considered as composite materials with a spatial periodic distribution of building blocks. In the case of CC those building blocks are submicrometric particles.

Here we will report on recent advances made in our laboratory to fabricate new colloidal crystals with the aim to find new optical properties in relation to PC. We will focus on the following novel topics:

(1) Non-close packed face centred cubic (FCC) structures by chemical etching techniques. Most results on solid colloidal crystals concern close packed systems. However, theory predicts that a non-close packed crystal structure presents stronger light scattering properties as compared to the close packed one. Here we shall show results on the fabrication method and optical characterization of non-close packed FCC colloidal crystals.
(2) Diamond structures made from nanorobotics. This technique helps to build up complicate 3D crystal structures not achievable, so far, from colloidal self-assembly methods. We will report on the construction method of a crystal aggregate with diamond symmetry.

Keywords: Colloidal crystals; Photonic crystals; Colloids; Inverse opals

Contents

1. Introduction

Interdisciplinary research is very fruitful in science. Great challenges in some field can be revisited in a new frame of reference with other expertises or methods that can help to find new solutions. This is what has happened between colloidal

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technology and photonic crystal challenges. I will focus this paper to show how the developments in colloid science have been of enormous help to achieve one of the major targets in the field of photonics. However, this is not only one-way information diffusion process. I will also show how the discoveries in Photonic Science and Technology can provide new scenarios and solutions to the development of colloids for applications in new devices.

Firstly, I will give a short introduction to photonic crystals. Then I will report about some of the strategies we have followed to achieve a colloidal crystal based photonic crystal with an omnidirectional gap. Then, I will show results on inverse opals. The self-organisation of colloidal particles is limited to close packed symmetries. However, I will show an easy processing method, to achieve photonic crystals with a non-close packed order.

Finally I will give results on the search of CC with a diamond ordering.

1.1. Photonic crystals and colloidal crystals: a brief historical introduction

PC is a new concept in the modern science that is bridging several fields as solid-state science, microelectronics and microphotonics [1]. The discovery of PCs has raised big expectations because it has been predicted (but not yet demonstrated) that it can be the new King Midas of the modern communication technology [2]. The most important argument for such great expectation is very simple. PCs work for photons as semiconductors do for electrons. They are formed from periodically distributed building blocks. However, at variance with semiconductors, those building blocks are much larger in size, in the sub-micrometric range. As a consequence of periodicity it appears strong optical interference effects very similar to what happens for electrons in silicon. In other words, it appears allowed bands and forbidden gaps for photons [3]. Therefore, PCs are also called as "semiconductors for photons". The great advantage of the photon over the electron is the absence of mass and electrical charge in the former one. If we were able to develop optical devices as diodes, transistors and switches, they would work much faster than silicon based electronic devices. This was the scenario after the seminal papers from Yablonovitch [4], and John [5] in the late eighties. The impact of PC discovery in science was so high that Maddox [6] wrote the following sentence in Nature, "If only it were possible to make dielectric materials in which electromagnetic waves cannot propagate at certain frequencies, all kinds of almost-magical things would be possible. . .." This sentence summarised the enormous relevance of PC in photonics and optoelectronics. It has triggered technological rush to achieve PCs with an omnidirectional gap and also to find applications in photonics.

However, as it often occurs in science, it has been claimed that this discovery was first reported by Ohtaka [7] in 1979. Also the technology to achieve a real three dimensional PC is not easy. The big challenge in PC technology concerns the development of a 3D microporous material with a periodicity value in the submicrometric region. Also the material should have a high refractive index value above either 1.8 [8] (for diamond structure) or 2.8 [9] (for FCC symmetry).

From all approaches and methods so far published, only two of them seem to show the best performances. The first one that concerns conventional lithography [10,11] has been used to construct a PC with a diamond structure with a limited number of layers. The second one is related to colloidal techniques. This one is very attractive as they may easily produce very stable and robust structures [12].

Here, I will report on the colloidal based methods we have developed to build PCs. I will consider two types of structures. Close packed CC based PC and non-close packed systems.

As colloids crystallise mostly in close packed symmetries it is necessary to make a further process to obtain PC with an omnidirectional gap. This process aims to increase the refractive index contrast of the microporous material. Also, the connectivity and topology of dielectric medium is important. In the case of FCC systems the inverse opal topology is the most suitable one. Inverse opal is the negative replica of a CC with a periodic distribution of air cavities surrounded by a high refractive index material.

2. Close packed colloidal photonic crystals

2.1. Colloidal crystal template

Most groups in the world have used as base material opals made by natural or assisted sedimentation of silica or latex micro-spheres onto flat substrates. This method gives rise to free standing, millimetre size polycrystalline pellets in which the beads show a clear tendency towards FCC packing. Analysis of the optical properties of these materials gave rise to a better understanding of PCs [13]. Also, CCs have been used as templates to obtain silicon [14,15] and germanium [16] PCs with inverse opal topology. The ability to grow crystals made of large particle size is important. One must properly choose the template lattice constant in order to guarantee that the PC properties appear at energies below the electronic absorption edge of the materials the lattice is made of. Fig. 1(A) shows the scanning electron microscopy (SEM) image of the cleft edge of a CC made of silica particles with a large sphere size (1260 nm) [17]. The image corresponds to a (1 1 0) facet of the PC. Spheres have been obtained with a modified Stöber method. We made the synthesis in a suspension of smaller silica particles that behave as seeds for the synthesis of larger particles. The settlement process of large particles into a solid colloid is different from that of small particles. In order to achieve a crystalline order, it was necessary to slow down velocity of sedimentation. Here we use a suspension of monodispersed particles (typically 1%) in a mixture of water and other co-solvents as ethyleneglycol. Also a further processing allowed extending their composition to a wide

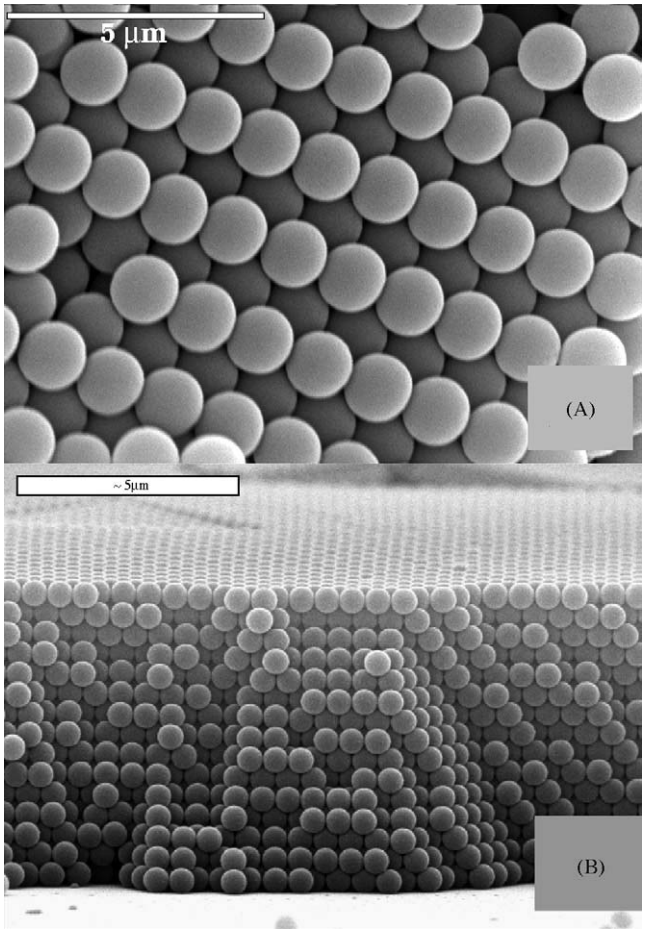

Fig. 1. (A) SEM image of the (1 1 0) facet of the cleft edge of a silica based colloidal crystal with a particle size of 1260 nm. (B) Thin film opal made from 620 nm latex spheres.

range of materials including polymers, and different oxides [18].

However, the optical quality of those lattices was largely diminished by the numerous intrinsic defects present in these samples [19], such as domain boundaries, vacancies, dislocations or cracks. New techniques to control the PC dimensionality have constituted a major advance in the search of defect free samples. One of those consists in placing a substrate such as a flat glass or silicon wafer in a vertical or close to vertical position within a colloidal suspension. Convection forces at the meniscus between the liquid phase and the substrate cause the formation of a thin film PC of well-defined thickness. Evaporation of the suspension medium moves the crystallization front downwards and large area crystals are created. This method developed by Colvin and co-workers [20], works well for silica and latex particles of diameter below 500 and 700 nm, respectively. Larger particle sizes have also been deposited by a similar procedure but under the assistance of heat convection forces [15]. A SEM image of a cleaved edge of a thin film opal obtained by this method is presented in Fig. 1(B) [21]. The thin film opal is made of latex particles. This technique is very sensitive to the shape of the meniscus, and, consequently, to both the nature of the suspension medium and surface properties of the substrate. Although the crystal thickness can be controlled by the concentration of particles in suspension, this method is not suitable to obtain very large crystals in a single deposition process. Another way to build large area planar opal films makes use of crystallization within two parallel plates. In this process, developed by Xia and co-workers [22], a sphere suspension is let flow between two parallel glass plates separated by a polymeric frame. The crystal thickness is now determined by the separation between these two plates or, in other words, the thickness of the frame. As the suspension flows within the cell, oscillatory shear is applied to increase the mobility of the particles and help them distribute uniformly. The suspension liquid finds its way out through openings realized in the polymer frame and the remaining confined crystal is let dry. The appropriate mixture of solvents permits crystallization of a wide range of particle between 200 and 800 nm [17].

PC technology has improved new techniques in the last years. One of them concerns the use of patterned substrates to growth CC either along different crystallographic directions [23,24] or to obtain PC wires and dots [25,26].

2.2. Close packed inverse colloidal crystals

In 1993, Sözuer et al. [27] predicted that under appropriate conditions, FCC PCs could present a full photonic band gap. Since then, many laboratories started a quest for methods to obtain inverse opals. As we mention above an inverse opal can be envisaged as the negative replica of an opal with periodically distributed air spheres in a high refractive medium. The essential condition to achieve a full gap is to synthesize an inverse opal with a transparent material in the optical region of interest, and also having a refractive index above 2.8 [9]. Furthermore, the amount of defects should be low enough to preserve the gap. Here we will give some important milestones of the inverse opal rush. Furthermore, we will summarize our contribution to fabricate silicon inverse opals that show the fingerprint of a complete full gap.

The first results on inverse opals came from laboratories with experience in colloidal crystal science. It concerns structures made of TiO_2 [28,29], carbon [30], II–VI semiconductors [31,32] and polymers [33]. However, those materials do not accomplish the essential criteria for complete band gap formation (i.e., a refractive index contrast above 2.8). Blanco et al. [14] and Míguez et al. [16] reported a method to infiltrate silicon and germanium within the void lattice of opals based on the chemical vapour deposition (CVD) of disilane (Si_2H_6) and germane (GeH_4), respectively. After infiltration, the silica scaffold is removed by hydrofluoric acid etching and the inverse structure is attained. Later on, Norris and co-workers developed an alternative CVD process to create high optical quality silicon inverse colloidal crystal films on top of silicon substrates [15]. Silicon is the best suitable material to build

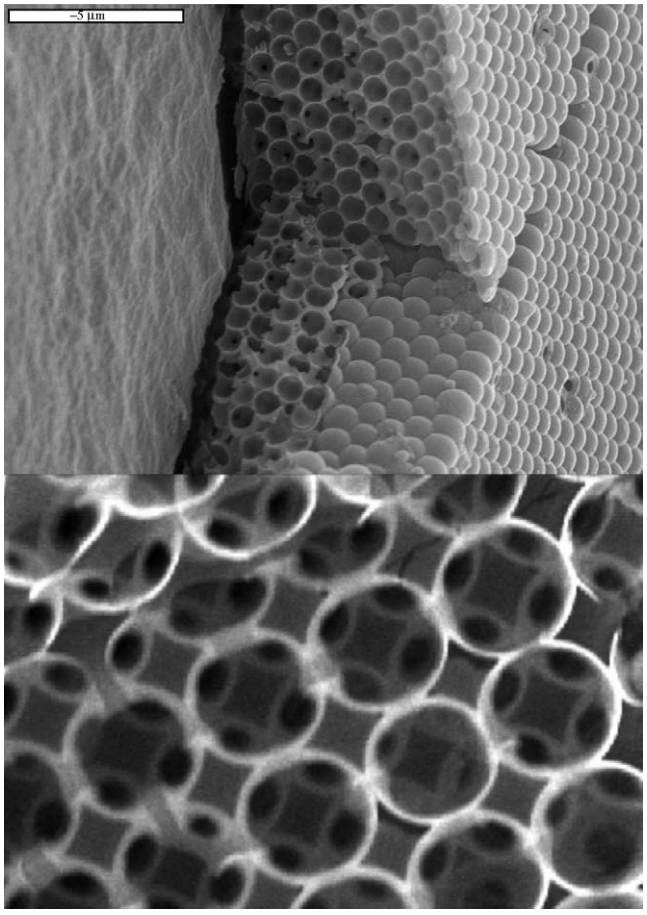

Fig. 2. Silicon inverse opal film (7 μm thickness), void diameter is 0.97 μm (above). Germanium inverse opal with a void diameter of 1.2 μm (below).

up a PC because it possesses a high refractive index ($n = 3.5$ for frequency values below the absorption edge) to guarantee the condition for a full gap appearance. Moreover, silicon is transparent in the region of 1.5 μm, the wavelength value for communication technology. Fig. 2 shows SEM images of a thin film silicon inverse opal (upper image) [17], and germanium inverse opal (lower image) [34]. By measuring the reflectance at different light incidence directions, it has been recently shown that such structure present a full photonic band gap [35].

A further control on the topology of the PC, as well as on the refractive index contrast, can be achieved by semiconductor multilayer infiltration. Alternate infiltration of silicon and germanium can be performed to obtain a Si–Ge multilayered coating, as it has been recently reported by García-Santamaría et al. [36]. In that work, the reaction time is the key parameter to control the amount of semiconductor loaded in the opal. Semiconductor layer thickness can be precisely controlled up to the nanometre length level. A subsequent selective oxidation and etching of the germanium layer can also give rise to interesting architectures like the one shown in Fig. 3. In that case, the continuous lattice of silica spheres is separated from a continuous lattice of Si shells by an air gap originated by the removal of germanium. Semiconductors heterostructures

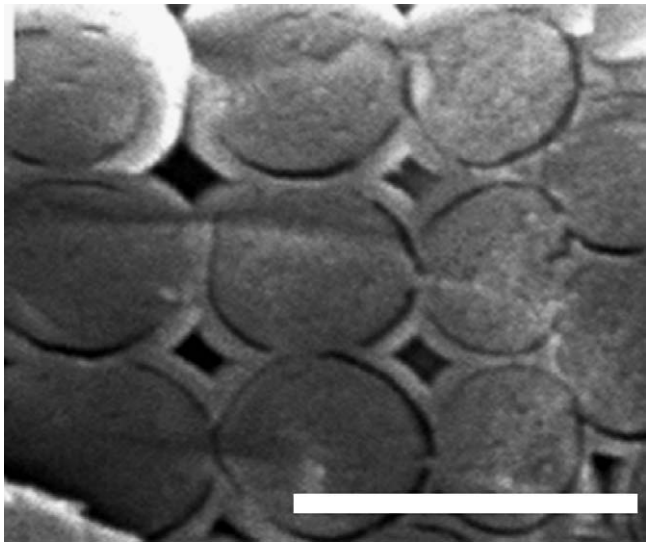

Fig. 3. Cleft edge SEM image of a silica-air silicon structure. The sample shows the continuous Si layer separated from the continuous silica, structure by air shell. The dark lines in the cleft edge are the air gaps between Si shell and the silica spheres of 0.66 μm of diameter. Scale bar is 1 μm (extracted from Ref. [36]).

provide, therefore, new ways to realise photonic band gap engineering in colloid based PCs.

3. Non-close packed colloidal photonic crystals

Close packed lattices for PCs have a problem in what it concerns optical properties. The omnidirectional band gap is small, even for restricted systems (as Ge and Si) that have very high refractive index values. Moreover, unwanted impurities, that usually appears in colloidal crystal templates, smears out optical gaps. Therefore it would be desirable to find alternative colloidal structures with better optical performances. Recently, Maldovan and Thomas [37] have made an extensive study of different crystal lattices derived from diamond lattice that can show full photonic band gaps. Non-close packed show wider gaps than those from close packed ones. Here we will show a simple chemical method to achieve a FCC non-close packed solid colloidal template. Finally, we will show a sophisticated method able to build up diamond opals system with the help of a nanorobot.

3.1. FCC non-close packed colloidal templates

In all the structures herein presented so far, nearest neighbour spherical particles (in the case of templates) or air cavities (in the case of inverse opals) are just touching, as they correspond to close packed structures. Also a sintering process makes spheres interpenetrate each other. Therefore, one can control the colloidal crystal volume fraction between 74% (for a close packed system) to 100% (when the air pores have disappeared completely). Here we will report some recently

developed techniques to modify the face centred cubic lattice topology.

A non-close packed FCC colloidal crystal can be attained combining colloidal self-assembly, thermal sintering and etching techniques. It results in an array of silica spheres interconnected through narrow tubular necks [38]. It allows tuning both the size of the particle and the neck diameter, thus providing a precise control on the lattice parameter, connectivity, porosity, and, consequently, photonic crystal properties of the silica sphere network. The method to fabricate these non-close packed opals includes two main steps. Firstly, the sample is fired at high temperatures to obtain an opal with a strong sphere overlapping; i.e., the opal void volume is strongly diminished. In second place, a severe etching process is achieved by immersing the sample into HF acid. As a consequence of the uniform etching process, opal porosity increases enormously and necks between particles are transformed into cylinders that connect neighbouring spheres.

Fig. 4(a) and (b) show SEM images of (1 1 1) and (1 0 0) facets of the processed opal. These pictures clearly show an opal structure in which the spheres are not any more in contact but bridged by tubular necks to their nearest neighbours. The longer the etching process, the smaller the sphere diameter and the longer and narrower the interconnecting blocks. The initial polydispersity of the spheres is most probably the cause of the absence of necks in several places. This new topology has a strong effect on the optical properties of these photonic crystals. In Fig. 5, we plot both theoretical band calculations (Fig. 5(a)) and the reflectance spectra of three samples (Fig. 5(b)), namely two non-compact opals with different void volume values (45 and 55%) and a reference sample with void volume value around the close packed one (19%). Reflectance experiments show Bragg diffraction peak obtained on the (1 1 1) free surface of the colloidal crystal. For the sake of clarity, we have calculated the lowest four bands for the samples with the extreme porosity values (19 and 55%). In all cases the nearest neighbour distance of spheres is kept constant to 460 nm. A clear widening of the Bragg peak is observed, as well as a blue-shift, as the sphere diameter (porosity) decreases (increases), in good agreement with band structure calculations [39], and also with simulated spectra profile employing the layer-Korringa–Kohn–Rostoker method [40,41] (dashed line plots in Fig. 5(b)). The higher intensity of the etched opals demonstrates that non-close packed structures present a stronger scattering than close-packed ones.

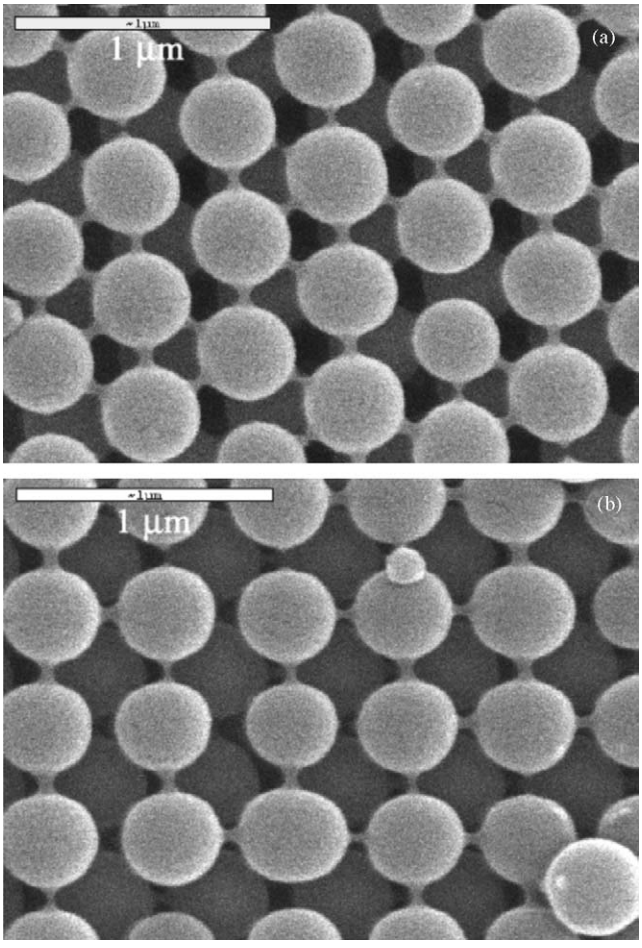

Fig. 4. (a) (1 1 1) and (b) (1 0 0) faces observed in the outer surface of an opal after a treatment involving sintering at 960 °C and acid etching for 20 min (extracted from Ref [38]).

3.2. Nanorobotic manipulation of colloids for diamond architectures

From all possible crystal lattices, diamond structure is the most paradigmatic one because it presents a wide and robust photonic gap [42]. Submicrometric particles can not be ordered in a diamond structure by standard colloidal methods, because the low filling fraction occupied by the spheres (36%) makes them quite unstable to be obtained by sedimentation methods.

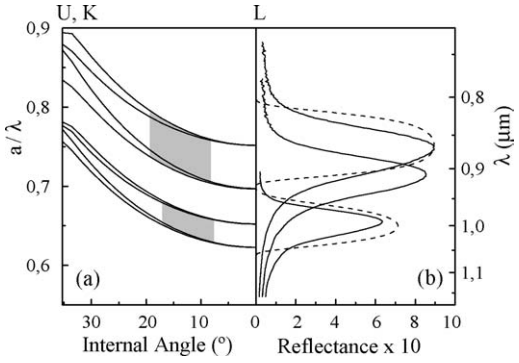

Fig. 5. (a) Band structure around L of two fcc sphere structures having a void volume fraction of 19% (four curves below) and 55% (four curves above). The shaded regions indicate the zones of the reciprocal space probed in the experiments. (b) Optical reflectance spectra (continuous lines) for three samples with void volume fractions of 19% (peak below), 45% (peak in the middle) and 55% (peak above). The corresponding theoretical spectra of the first and the latter of those, calculated by the KKR method, are shown as dashed lines (extracted from Ref. [38]).

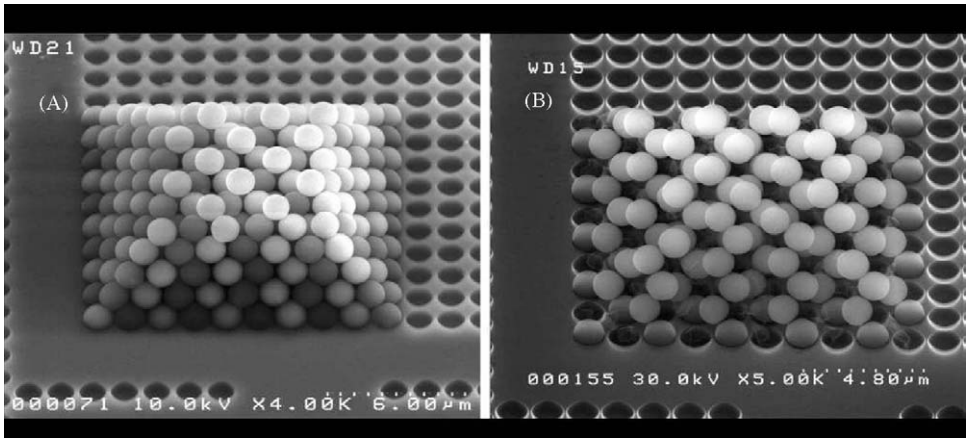

Fig. 6. (A) Body centred cubic lattice of 1.18 nm silica and latex spheres on a silicon template made of holes periodically distributed in a square lattice. (B) Diamond lattice of silica spheres after selective etching of latex particles (extracted from Ref. [46]).

New techniques, based on trapping of micrometric spheres by radiation pressure [43,44] or atomic force microscope [45] to handle single particles can be useful to build up non closed packed 3D structures. Recently, a patterned Si wafer surface was used to build, for the first time, a diamond colloidal lattice. The construction of a diamond structure is based on a simple fact. A body centered cubic (BCC) lattice is formed by two interpenetrating diamond lattices [46]. Therefore, the proposed route comprises the assembly of a BCC lattice of mixed silica and latex spheres of equal diameter and the removal of the latex subset. Silica spheres would sit in the positions of one of the interpenetrating diamond lattices while latex ones would lay on the other sub-lattice. The resulting structure, after latex removal, is a diamond lattice made of silica spheres [46].

Different silicon templates, with triangular and square arrangement of circular holes, have been used to construct BCC lattices along (1 1 1) and (1 0 0) directions. The dimension of holes and their periodicity have been precisely designed and fabricated according to the bead size. A nanorobot attached to a SEM was used to pick up the beads, and build a latex-silica colloidal crystal arranged in a BCC lattice by placing them at the predefined sockets on the silicon patterned substrate (first layer), or at the appropriate position in a stable location among the supporting spheres from the layer underneath (other layers). Fig. 6(A) shows the SEM images of a BCC latex-silica arrangement build up along (1 0 0) crystallographic direction, the total number of layers being six. Then, diamond structure is obtained when latex particles have selectively been removed. Plasma etching has revealed as a good method to gently remove latex and it hardly affects the silicon wafer or silica. Fig. 6(B) shows the resulting diamond crystal after plasma etching.

4. Perspectives

It is my impression that the state of art of PC based colloidal crystals is still crude for applications in communication technology. It would be necessary to increase the optical quality of PCs. The main bottleneck concerns the control of the number unwanted defects. Defects in a material with a high refractive index induce strong optical scattering effects that smear out the PC performances. Also it would be necessary to find methods to produce large-scale (of the order of centimetres) samples for mass fabrication. However, the developments so far achieved can be of application in other fields of science and technology where no such a high optical perfection is needed. Very recently Mallouk and co-workers [47] have shown that PC architectures increase substantially the efficiency of photoelectrochemical solar cells [48]. The group velocity of photons is dramatically slowed down at frequency values near photonic gaps. Therefore, localization effects enhance photovoltaic process. Also, Holtz and Asher [49] have demonstrated that PCs can be applied to biosensors. In this case, colloidal crystals made from hydrogel dramatically changes their optical properties when they detect the presence of glucose.

All those applications come from the astonishing different optical properties that PC can show. Therefore one can speculate that PC crystals can also be of application in any other discipline where optical properties or optical assisted processes play important role, as photochemistry, biophotonics, etc.

In summary, I have shown several examples of PC architectures that have been achieved with the crucial help of the very active field of colloidal science.

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