Colloidal crystals for photonic applications

Author: Ana Valdés Prats
Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.*

Abstract: Nanoparticles of silica were synthesized by a sol-gel process and were analyzed using Scanning Electron Microscopy (SEM). Langmuir-Blodgett (LB) technique was applied for self assembling the silica nanoparticles in a closely-packed hexagonal 2D structure and transferring them on glass and c-Si substrates. The morphology of the resulting 2D photonic crystal was studied by Atomic Force Microscope (AFM). Finally, their optical characteristics were determined by UV-vis transmittance.

I. INTRODUCTION

A colloidal crystal is an ordered array of recurrent sub-micrometric particles forming a photonic crystal (PhC), which consists of a periodic arrangement of a dielectric material (in our case monodispersed nanoparticles) that exhibits strong interaction with light. This periodic structure controls photons such as a periodic potential in solid state controls electrons. In particular, PhC has a photonic band gap in which all optical modes are forbidden. The most common example of a natural photonic crystal based on particles is a semiprecious jewel called opal. In 1964 J.V. Sanders analyzed the internal structure of a natural opal and found out that it was formed of amorphous silica spheres which showed a tendency to be organized in cubic centre face structure [1].

The most important first investigations about photonic crystals were carried out by Eli Yablonovitch and Sajeev John [2], who proposed to inhibit the light inside a material. Previously, in 1887 Lord Rayleigh studied that a wave could refract totally when this one went through a periodic material. But the concept of photonic crystal was first introduced by Othaka in 1979 [3].

In 1989 E. Yablonovitch and T. J. Gmitter made the first structure with a photonic bandgap consisting of spherical holes arrayed throughout a block of plastic in a face-centered-cubic (fcc) pattern [1]. After that, Thomas Krauss, who made the first demonstration of a two dimensional photonic crystal at optical wavelengths [4], and Shkunov et al., who performed studies on photonic devices, developed other new photonic crystals [5].

Nowadays, the interest of making materials capable of controlling or manipulating the flow of light and that it can focus on specific regions has increased. In fact, the first commercial products involving two-dimensionally periodic photonic crystals are already available in the form of photonic-crystal fibres. In summary, they can be used in several applications, such as optical switches, physical, chemical and biological sensors.

There are two methods to synthesise nanoparticles: top-down and bottom-up. The first one, in general, is not interesting because the obtained particles have different sizes. The bottom-up is classified in two types: gas-phase synthesis and liquid-phase synthesis. The techniques for gas-phase synthesis are: vapor jet refrigeration, thermal evaporation, sputtering, chemical vapor deposition (CVD) and laser ablation. The techniques for liquid-phase synthesis are: solvothermal synthesis, microemulsions and sol-gel. This last process, also called Stöber-Fink-Bohn, has been used in this work to synthesize silica nanoparticles. This process is commonly used because it provides a simple, economic and effective method to produce high quality coatings.

Moreover, these particles could be organic spheres, as polymers (such as polystyrene), or inorganic spheres like silica, which are the most commonly used. Silica nanoparticles are colloidal particles and, in this work, we have studied their morphology and distribution by the imageJ 1.47v program [6] from images obtained by scanning electron microscope (SEM).

There are different methods to organize colloidal particles. In this report we will describe up to four methods, which are considered interesting to obtain a photonic crystal. However, only one has been used. The first one is to making three dimensional photonic crystals. This technique consists of depositing monodisperse colloidal particles, by the effect of the gravity force on a flat substrate. The second one consists of an immersion of a substrate in colloidal dispersion with controlled temperature and humidity. Thereby, the evaporation of the liquid phase propels the spheres to be accumulated on the meniscus suspension. This technique is called evaporation induced self assembly (EISA). The third one is spin-coating, which consists of the acceleration of a liquid puddle on a rotating substrate. This technique is very fast and in some many cases good results can be obtained. The last one is the Langmuir-Blodgett technique (LB). Initially, the main idea of this method is to form a monolayer of an amphiphilic substance (Langmuir layer) on the water surface and then transfer it to a solid and flat substrate (Blodgett method). For particle self-assembling experiments, the amphiphilic substance is substituted by monodispersed nano or submicrometic particles. The LB technique has advantages over previously reported techniques, such as high reproducibility, formation of large area films with low cost and capable of producing a large number of hexagonal close pack nanoparticles layers at a single process.

Finally, depending on the characterization performed (morphological, optical) we should choose the most suitable substrate. The most common substrates are glass, silicon, quartz and mica. Glass and crystalline silicon were used in this work. Glass was used to measure the transmittance and crystalline silicon to take images by AFM.

II. THEORETICAL FUNDAMENTALS

Photonic crystal (PhC) is a material with a modulation of the refractive index in one, two or three spatial directions, classifying the PhC's in onedimensional, bidimensional and

* Electronic address: avaldepr7@alumnes.ub.edu

threedimensional. This modulation of the refractive index is due to the repeated structure formed by particles, dots or layers embedded in other materials (air or dielectric). So, when photons go through a structure, for example of particles embedded in air, they find regions with high index refraction, particles, and low index refraction, air. This interface between mediums with different index refraction causes reflexions and interferences. This phenomenon is known as Bragg diffraction:

$$m\lambda = 2d\cos\theta_{int} \qquad (1)$$

where λ is the photons wavelength, d is the interplane distance and θ the intern angle of the propagation of the light. The factor m is an integer associated to the order of diffraction (0, ±1, ±2, ±3,...).

The existence of Bragg diffraction on specific frequency (ν) or wavelength ranges causes that photons of other wavelength ranges cannot be transmitted. This leads to forbidden frequency bands often termed as photonic bandgaps. In fact, no available photonic states for these energies, and for this reason forbidden bands of energy ($h\nu$) appear. Due to this, photonic crystals have iridescences and change the colour depending on the illumination angle. Aversely to what happens in other materials, the absorption of determinate wavelengths defines the colour.

A PhC is defined by the following parameters:

- Lattice parameter. The photonic bandgap depends on it, so the size of the particles is relevant. Modifying the size is the same as breaking the periodicity in a silicon crystal on a semiconductor, then the electrons undergo a different periodical potential.
- Crystalline structure. It describes the high structural range. It is formed by Bravais lattices and the base.
- Topology. There are two types of topology: cermet topology and network topology. The first is a discontinuous topology of separated clusters in a matrix and the second is created in a form of interconnected spherical grids.
- Void fraction (f_v) is a fraction of the volume of voids over the total volume, between 0 and 1.
- Geometry of the dispersion centres. The shapes of the dispersion materials can be spheres, cubes, cylinders, etc.
- Refractive index contrast. Difference between high and low refractive index from the two mediums. The higher the contrast is, the more notable properties are.

In this work, the crystalline structure is a hexagonal bidimensional (2D) array of spheres. The two mediums are air and silica nanoparticles. So, the dispersion centres are spheres of silica in a cermet topology.

III. EXPERIMENTAL PART

The experimental part was divided in two parts: Firstly, the nanoparticles were synthesised by the sol-gel process and secondly they were deposited on crystalline silicon wafers and glass substrates by the Langmuir-Blodgett technique.

However, first of all cleaning all the tools properly was very important. They were cleaned using acids and ultraclean water.

The mixture of acids used is called Piranha. This acid removes organic residues of the objects to be immersed into LB trough. Piranha is prepared with a 3:1 mixing concentrated sulphuric acid (H_2SO_4) with 40% (vol) and hydrogen peroxide solution (H_2O_2). After the acid, all the material is rinsing with deionised water. Finally, in order to eliminate all the remaining water of surface it is dried with a nitrogen jet.

Hydrofluoric acid (HF) was also used to clean to clean the syringe, used to extract the nanoparticles solution and spread them on the water surface of the LB trough.

Depending on the material it is very important not to let the acids act during a long time. For instance, with HF it is necessary a maximum of 5 minutes, and also Piranha with metals.

It is compulsory to use acid special gloves, wear glasses and a lab coat to manipulate chemicals. The cleaning process is performed under a hood. Then, the residues are thrown in the corresponding containers.

The glass substrate is also cleaned with Piranha, but not c-Si substrate.

Finally, the troughs of the LB equipment are cleaned with a dilution of detergent in ultrapure water, rubbing the surface using vinyl gloves.

A. Silica nanoparticles synthesise

The procedure followed to synthesise (Stöber-Fink-Bohn method) the silica nanoparticles was the next:

First the precursor of tetraethylorthosilicate (TEOS, 98% purity, Sigma-Aldrich) was diluted in ethanol (99,8% purity, Panreac) and stirred at 350 rpm for 10 minutes. Then, without stopping the shaker, the ammonia (NH_4OH, 28-30%, Sigma-Aldrich) was added to the solution and it was left for 15 minutes. After this time, the ultrapure water was added. Then, in order to disperse conveniently the formed particles, a surfactant like a Aminopropyltriethoxysilane (APTS, 99%, Sigma-Aldrich) was added and left the resulting solution for 22 hours stirring.

In order do not contaminate the solution and to avoid exposition to atmospheric water (solution is hygroscopic), the solution was covered all the time and it was only opened when the products were added.

After 22 hours, without stopping the shaker, the solution was heated at 65 °C for one hour and a half.

The purpose of the chemicals used while stirring, was:

a) TEOS was the precursor to silicon dioxide.
b) Ammonia carried out a catalytic action and was the responsible to begin to create the nanoparticles.
c) Ultrapure water was used to produce the hydrolysis to the system ethanol/TEOS.
d) APTS was the surfactant which provided hydrophilic properties to the sub-micrometric particles, this was due to the fact that the nanoparticles had a higher density than the water.

B. Nanoparticles deposition

The Langmuir-Blodgett equipment that was used (KSV 5000 equipment) consists of two troughs of 71x12 cm each

one made of PTFE. In this experiment, only one of the troughs was used. Troughs should be filled to the brim with ultrapure water (ultraclean electronic grade deionised water, ρ = 18.2 MΩ). Other accessories are, two pairs of barriers for the compression and two Wilhelmy balances for monitoring the surface pressure of each trough. The balances consist of a little sheet of platinum touching the water surface and hanging from a torsion balance (the accuracy of this balance is 0.1 mN/m). Pt sheet can be cleaned heating it with a lighter. The surface pressure is a physical parameter very important during all the experiment; depending on its value the particles can be dispersed or accumulated, and so the resulting particle monolayer becomes dispersed or conveniently compacted or overlapped. Substrate is attached to a rotating dipper head for its positioning over the adequate trough.

In order to protect LB equipment of the vibrations, dust and the air waste, it is placed on a solid aluminium plate and inside a cabin made of aluminium and glass.

All the LB experiment is controlled by a computer programme.

Before the compression, the c-Si and glass substrates were vertically positioned together back to back on the hook and immersed all both into the ultrapure water of trough.

Sub-micrometric particles should be also prepared before compression by LB:

After nanoparticles synthesise (section above), they were put into the centrifuge at 1.4x1000 rpm for 25 minutes. After the centrifugation the nanoparticles stayed at the bottom and the ethanol over it, so it was possible to throw the ethanol away. Then, it was added methanol and put on the vortex mixer. The purpose to put it inside the shaker was to pull up the nanoparticles from the bottom and mix them well with the methanol. Later on, it was added the Chloroform and the same process was repeated.

Ethanol and chloroform produce the homogenization, so they have two complementary functions: methanol causes aggregation and chloroform dilution. On this step, the solution can be added to water, because chloroform and water separate in two phases and the particles stay in the layer of chloroform.

The LB experiment started after the above mentioned. It was taken with the syringe 2.5 ml of the solution and then put it drop to drop in the ultrapure water surface on the first trough. Then, it took 25 minutes to allow the evaporation of the solvents (methanol and chloroform). After this, the compression started with the barriers moving on a constant velocity, 5 mm/min. The compression process ended up when the curve reached the 10.5 mN/m.

After that, nanoparticles were transferred to the substrates (deposition process) lifting the dipper at 2 mm/min.

All the experiment took one hour and a quarter.

IV. RESULTS AND DISCUSSIONS

A. Silica nanoparticles

Morphology (diameter and roundness) of the silica nanoparticles from solutions 1 (S1) and 2 (S2) have been studied using the program imageJ.

S1 and S2 were obtained using the same chemical products but adding it slightly different amounts for each solution.

The results of the diameter and roundness distribution for 76 nanoparticles from the S1 and for 152 nanoparticles from the S2 are shown respectively in figure 1.

To obtain these data, figures 1 (a) and (b) have been processed by different masks. For that, background, threshold adjust, a binary process and removed outliers have been considered. The measures of the diameters refer to Feret's diameter.

Then, the two distributions have been obtained using the frequency function in MS Excel.

To properly calculate the diameter and roundness correctly the particles of the edges have not been considered. The circularity and solidity are not shown because after processing image the calculated results are worst than the real image.

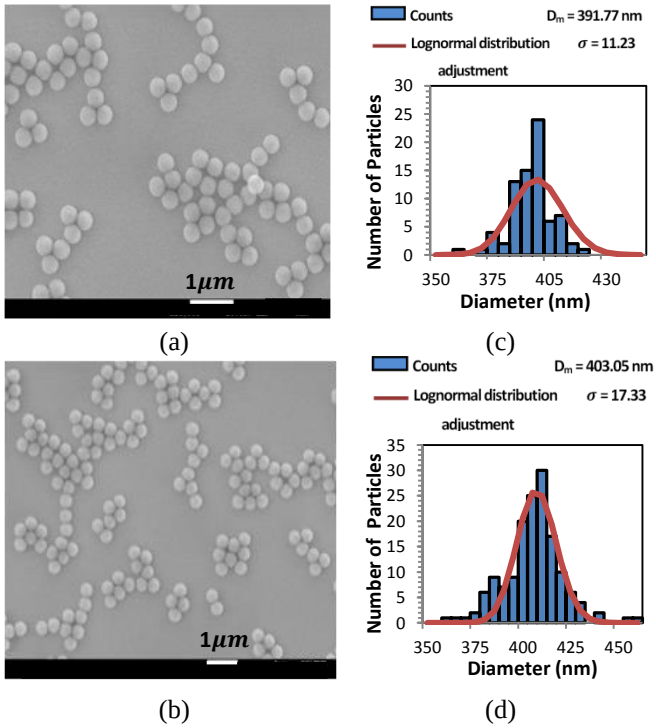

FIG. 1. (a) and (b) Silica nanoparticles resulting from samples of the solutions 1 and 2 respectively deposited on silicon substrate by spin-coating and taken by SEM. (c) and (d) Histograms of the silica nanoparticles diameters for the solutions 1 and 2 respectively.

As seen from figures 1 (c) and (d) nanoparticles follow the lognormal function. If it had been performed with a major number of particles, this function would have completed all the histogram.

Data, obtained with the lognormal function, were treated thanks to Excel Solver, which finds the value of the parameters minimizing the root mean square error. Lognormal function formula data have been calculated thought optimizing two parameters, mean diameter and standard deviation.

Moreover, it is observed that in solution 2 there is more nanoparticles diameter dispersion, moreover nanoparticles roundness is better than solution 1. Because of this, nanoparticles of solution 1 have been used to synthesize the photonic crystal.

The results that it has been mentioned are listed in this table:

Particles solution	Average diameter (nm)	Average roundness
S1	392 ± 2	0.956 ± 0.03
S2	403 ± 2	0.913 ± 0.03

Table I: Average Diameter and average roundness of the SiO_2 nanoparticles from the solutions 1 and 2.

B. LB film deposition

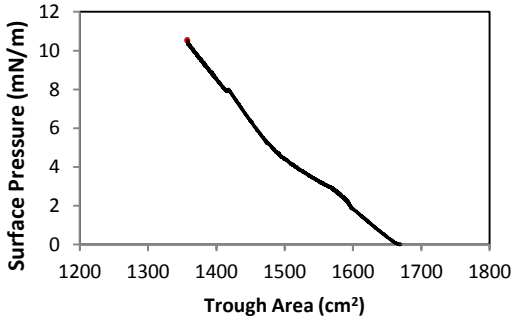

FIG. 2. Surface pressure vs trough area. Red point: surface pressure of collapse.

It is observed a pronounced slope. From the very beginning, the surface pressure rose quickly. Due to this, the control of the speed barriers in the experiment was very important not to produce aggregation, i.e. at range of 1600 cm^2 the velocity of the barriers was lowed from 5mm/min to 0.5 mm/min. The surface pressure of collapse was at 10.5 mN/m.

The monolayer, resulting of SiO2 nanoparticles deposition, has been observed by AFM:

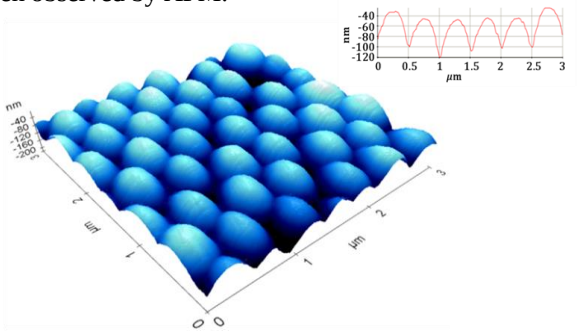

FIG. 3. Morphology of 3 μm x 3 μm area from the silica particles monolayer on the c-Si substrate, studied by AFM. Top: Surface profile.

In figure 3, nanoparticles were observed forming to the typical hexagonal structure. Nevertheless, not all of them have been fitted perfectly and it seen some voids among them.

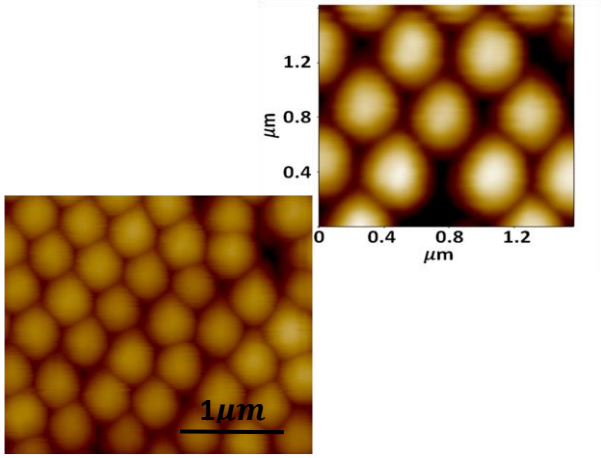

FIG. 4. AFM image of the silica particles monolayer and one of its domains.

In figure 4, it is observed that not all the nanoparticles touch each other, for instance there is space between two nanoparticles at the bottom.

C. Transmittance

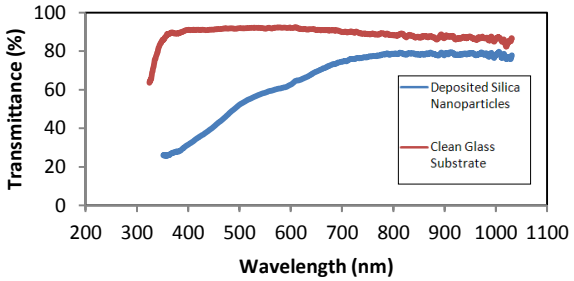

FIG. 5. Transmittance representation of the 2D photonic crystal in the normal direction.

It is observed that the transmittance of the SiO_2 monolayer drops to 30% between 400 nm and 700 nm. This is caused by the diffraction.

No peak to show the gap position is observed. This fact might be cause by the dispersion of the nanoparticles diameters.

D. Band Structure

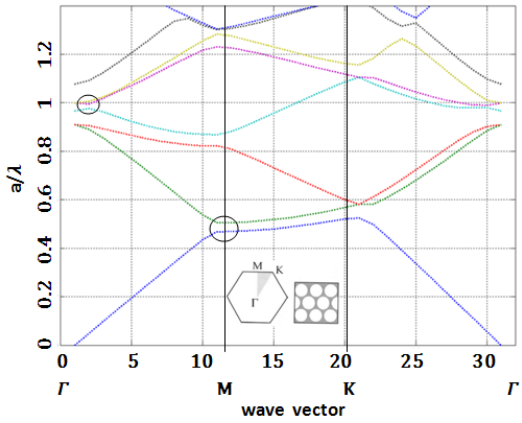

FIG. 6. TM: Band Structure of a 2D triangular photonic band structure. The circles indicate the pseudogaps in the ΓM direction. Inset: the first Brillouin zone of a hexagonal lattice.

Physical characteristics of the 2D photonic crystals allow the electromagnetic waves propagation inside them to be divided in to two modes, TE and TM. In this section, it is studied the second one.

Figure 6 corresponds to triangular lattice with SiO_2 spheres in air. This TM band structure was obtained by a Matlab code from Shangping Guo [7].

The expression of the volume fraction is $f = \frac{4\pi R^2}{3\sqrt{3}a^2}$. The radius, *R*, of the spheres has been taken the same as nanoparticles radius and the dielectric constant of silica spheres is $\varepsilon = 2.04$.

There are two pseudogaps for TM mode in the ΓM direction, the first one from 0.975 to 0.995 between fourth and fifth band, and the second one from 0.468 to 0.505 between first and second band.

Moreover, assuming the lattice parameter constant, it has been observed that if nanoparicles diameter decrease, the a/λ value increase.

E. 2D Photonic crystal

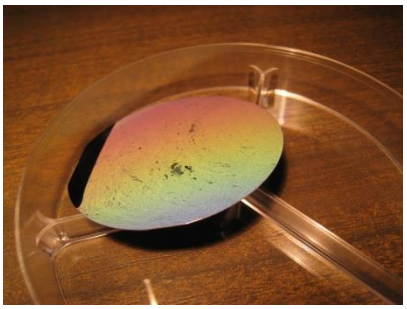

FIG. 7. Image of the silica nanoparticles deposition result on a c-Si substrate.

Figure 7 shows the 2D photonic crystal obtained. Iridescences can be clearly seen. Actually, blue, green, red and a little of yellow colours can be clearly seen too.

The fact of noticing the colours shows that de deposit has successfully been made.

V. CONCLUSIONS

- Nanoparticles were synthesized by the sol-gel process. Nanoparticles from solution 1 were better than solution 2. Since images obtained by SEM showed that the nanoparticles from solution 1 had more roundness and without aggregations.
- The monolayer was performed by the LB technique. On the one hand, the bulk monolayer showed a uniform one. On the other hand, images from AFM showed defects like voids and misaligned particles. However, it was observed that, in general, nanoparticles were organized in typical hexagonal structure.
  Defects might be caused by different factors: depending on the time taken to evaporate the solvent, the value of the compression when it was formed the monolayer, also capillarity forces can affect this process, and finally, a little increment of the amount can affect, for instance, hydrophilic properties of nanoparticles.
- The transmittance of the SiO_2 monolayer showed that the range between 400 nm and 700 nm the transmittance decreased. This fact is due to a loss of energy in the normal direction, it is caused by the diffraction. Besides, it didn't show a peak or peaks corresponding to the bandgap. This fact is due to the dispersion of the nanoparticles diameters and, also, to some defects, like voids, on the monolayer.
- The optical properties of a photonic crystal can be modified, changing the parameters, refractive index and lattice parameter. These parameters can be controlled at the very moment of photonic crystal manufacturing.
- In conclusion, nowadays it is being studied a lot about photonic crystals and especially about how to reproduce the same perfect periodicity that it is found in nature. The rhythm of these investigations indicate that in a few years there will be some useful applications like photonic crystal lasers, photonic crystal wave guides and electronic components based on photonic crystals.

Acknowledgments

I would like to express my gratitude to my supervisor, Dr. Enric Bertran, whose expertise, understanding and patience, added considerably to my graduate experience.

I would like to thank Edgar J. Cabrera for the assistance he provided me at the experimental stage.

Finally, I thanks the Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB) for the devices.

[1] K.Sakoda, "Optical properties of photonic crystals", Springer-Verlag, Berlin (2005).

[2] E.Yablonovitch and T.J. Gmitter, "Photonic Band Structure: The Face-Centered Case, "Physical Review Letters, Vol. 63, No. 18, 1989, pp. 1950-1953.

[3] K.Othaka, Phys. Rev. B 19 (1979) 5057.

[4] T. F. Krauss (1996), "Two-dimensional photonic-bandgap structures operating at near-infrared wavelengths", Nature 383 (6602): 699–702.

[5] J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, T. Alfrey, J. Polym. Sci. 20, 225 (1956).

[6] Image Processing and Analysis in Java. Wayne Rasband National Institutes of Health, USA.

[7] http://www.phys.ubbcluj.ro/~emil.vinteler/nanofotonica/PWM/pwmmanual_Guo.pdf