Photonic Glass: A Novel Random Material for Light**

By *Pedro David García, Riccardo Sapienza, Álvaro Blanco,* and *Cefe López**

From medieval stained glass windows to future photonic chips, understanding light interaction with complex dielectric media has been the key to design and tailor the optical properties. From random to periodic media, the engineered internal microstructure of a dielectric is at the basis of many new optical properties which are unexpected in homogeneous dielectric media. Very promising examples are represented by "left-handed" materials which show negative values of permeability and permittivity,[1,2] and for which light propagation, Doppler effect, Cherenkov radiation, and even Snell's law are found to be strongly affected. Another important example is given by photonic crystals,[3,4] where the dielectric function (ε) varies periodically on the length scale of the light wavelength, and which exhibits anomalous refraction,[5] super-refraction (superprism effect),[6] small group velocity,[7] and, for certain structures, even the opening of a complete photonic bandgap (PBG).[8] In both cases, the nanometer and micrometer sized building blocks are arranged periodically to induce the required properties.

Usually, defects in photonic crystals are regarded as undesirable features that spoil optical quality and performances. However, they can also be viewed as an enriching factor since, when controlled, they can be used to build up cavities, waveguides etc. being the base of future circuits of light. This only happens when a strict control is exerted on defects amount, position, shape, and other morphological characteristics. The amount of defects in photonic crystals produced by self-assembly is partly out of control and the achievement of the highest quality possible is a common goal of the colloidal community, for which many routes have been tested.

Disordered microstructured dielectrics, which are based on an opposite assembly strategy, are a rich and novel photonic medium. Random packing of hard spheres has been focus of considerable attention[9] for the last decades as a model to pack objects efficiently. Nevertheless, the packing of spheres is, apparently, the exception rather than the rule showing the highest possible filling fraction.[10] A number of interesting new optical phenomena have also been studied in random media such as coherent backscattering enhancement,[11,12] Anderson localization of light,[13–16] random lasing[17–19] only to mention a few. Three-dimensional random systems have been mainly achieved by the use of very polydisperse distributions of different materials powders or clusters.[20] A random distribution of monodisperse building blocks forming a solid phase has not yet been achieved. Using spheres, which has been tried in colloidal suspensions,[21] offers a very interesting advantage as they are the simplest object for which light resonances. Moreover, the interaction between light and a dielectric sphere can be described completely by Mie theory, an exact solution of the Maxwell's equations. Some experiments have been already performed in a single[22] or a small group[23] of micro-spheres. A new range of interesting phenomena will be affected by monodispersity of spheres, giving rise to a resonant behaviour[24,25] of diffusion constant, transport mean free path and energy velocity or random lasing action in macroscopic arrangements of this kind of scatters.

In this work, we present a new material that we call "photonic glass". This new three dimensional system is composed by monodisperse polymer spheres arranged in a completely disordered (random) way. Due to the resonant behaviour of the spheres, discrete light states exist, and therefore every sphere acts as a meta-atom[26] for light. We describe two different approaches to grow completely random distributions of monodisperse polymeric spheres with diameters from 200 nm to 2300 nm. The first method is based on rheology and takes advantage from the two-body interaction between polymeric spheres in colloidal suspensions. Very thick (from a few hundred microns to millimetres) and uniform samples can be grown attenuating the sphere-sphere repulsive potential by dissolving a low concentration of electrolytes (ions) in the colloidal suspension. The second method is based on vertical deposition,[27] which is commonly used to grow colloidal photonic crystals providing extremely high quality structures. By combining a binary colloidal suspension composed by polymethyl methacrylate (PMMA) and polystyrene (PS) spheres and by selective etching of one of them, thin disordered films can be grown.

Contrary to intuition, the introduction of arbitrarily high amounts of disorder is an unsuspected equally difficult task as obtaining defects-free systems. Few methods were tested here to get a completely disordered arrangement of monodisperse spheres such as rapid sedimentation or modified vertical deposition, being completely unsuccessful. Only the two methods presented here after were found to be fruitful.

[*] Prof. C. López, P. D. García, Dr. R. Sapienza, Dr. A Blanco
Instituto de Ciencia de Materiales de Madrid (CSIC) and
Unidad Asociada CSIC-U. Vigo
C/Sor Juana Inés de la Cruz 3, 28 049 Madrid (Spain)
E-mail: cefe@icmm.csic.es

A charged colloidal suspension is basically a mixture of colloidal particles such as polymeric microspheres and small ions, the electrolytes. The study of the stability of such a system has a long history[28,29] and a large degree of complexity due to the intrinsic many-body nature of the Coulomb interactions involved. A very recent work in this field[30] describes very accurately the early stage coagulation of a charged colloidal suspension. The two-body sphere-sphere potential of an aqueous colloidal suspension of charged spheres with diameter d and charge Z_0 in presence of point like electrolytes with charge Z_i and numeric density ρ_i can be expressed as a sum of two terms: $U(r) = \phi(r) + U_{vdw}(r)$, where $\phi(r)$ is the electrostatic repulsive potential and $U_{vdw}(r)$ is the attractive Van de Waals potential. In a non-charged colloidal system, $U(r)$ represents a potential barrier which prevents colloids from flocculation. Briefly, the presence of electrolytes attenuates $\phi(r)$. The interaction between two spheres is so sensitive to the presence of ions even to transform the initial repulsive potential into a totally attractive potential. A salt concentration of 10^{-2} M is enough to force the polymer colloids to flocculate, breaking the initial stability of the system. Once the microspheres coagulate forming disordered clusters and falling down in the colloidal suspension, it is impossible to order them. We take advantage of this very well known fact in colloidal systems to grow completely disordered random distributions of monodisperse polymer microspheres with a fine control over the thickness of the sample.

Figure 1a shows scanning electron microscopy (SEM) images of sample of 780 nm PS spheres grown by this method. In this case, very uniform, with areas of few square millimetres and thicknesses of some 100 μm (see inset of Fig. 1a) photonic glasses can be grown with, in principle, a random distribution of monodisperse spheres. Here we obtain filling fractions $f \sim 0.5$, which can be estimated by weighting the samples when their geometry is known. For random close packing of monodisperse spheres the theoretical[10] filling fraction is 0.64. It is important to point out that, although this system has been extensively studied and well reported theoretically, to our knowledge it has not been reported experimentally. Samples like the one shown in Figure 1 represent the closest ever reported to random close packing of monodisperse spheres.

An alternative way to grow a disorder distribution of monodisperse spheres is what we call alloy colloidal crystals. To do that, binary colloidal suspensions of PMMA and PS spheres were ordered by vertical deposition.[27] Once the alloy colloidal crystal is synthesized, we apply a chemical selective etching of one of the two kind of spheres which composed the crystal. In particular, we use Cyclohexane to selectively dissolve PS. Varying the diameters ratio between both kinds of spheres, different disordered systems can be grown.

An optical and morphological study of disorder in the resulting mixed PS-PMMA samples has already been reported,[31] but only in very polydisperse systems. Our aim is to have monodisperse disordered thin films. For that purpose, PS spheres were selectively dissolved with Cyclohexane leaving PMMA intact. Two kinds of disordered systems can be ob-
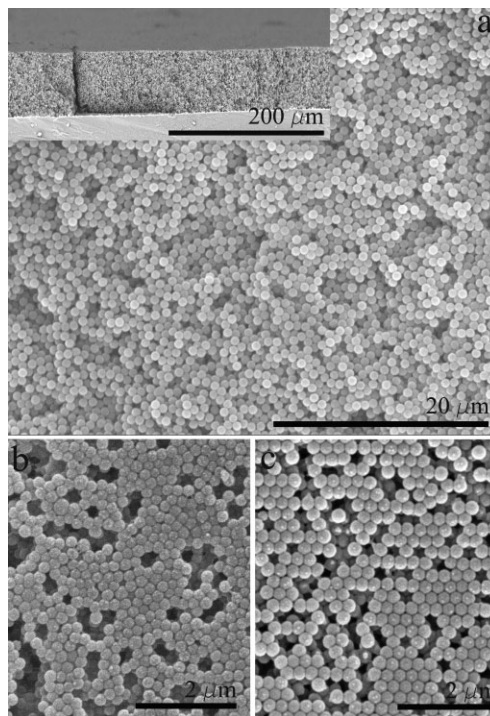

Figure 1. a) SEM images from a photonic glass surface. The inset shows a cleaved edge of a photonic glass. b) Thin disordered film grown by vertical deposition with PS and PMMA spheres with different diameter (457 nm and 260 nm, respectively). c) Thin disorder film grown by vertical deposition with PS and PMMA spheres with the same diameter (260 nm). The vacancies are the original positions of the PS spheres before selectively etching them with Cyclohexane.

tained. If the spheres diameters are initially different, the resulting system is a random and disordered thin film composed by PMMA spheres (Fig. 1b). On the contrary, if the spheres diameters are initially equal, a different kind of disordered system is obtained. SEM Figure 1c shows an alloy colloidal crystal initially composed by 30 % of PS spheres and 70 % of PMMA spheres after PS etching. The resulting system is a vacancy doped colloidal photonic crystal, where the amount of vacancies is determined by the initial relative concentration of PS-PMMA spheres in the initial colloidal suspension and their positions are random. These samples have typically the dimensions of a colloidal photonic crystal grown by this method, that is, few microns thick and few centimetres wide. It is worth mentioning that the homogeneity of the resultant structure after etching which might be useful to control disorder by, for example, adding very small amounts of dopants (vacancies) one could build up systems where random or unwanted defects could be tested in a controlled manner.

To measure the amount of remaining order, optical tests are conducted where specular reflectance (R) and transmittance (T) are measured. When the material composing the colloidal particles is transparent (i.e., not absorbing) and the wavelength involved is larger than the particles, the magnitude $R+T$ can be used as a measure of the order.[32,33] Optical spec-

troscopy (Fig. 2) and the image of the autocorrelation function (Fig. 3) were performed to analyze the degree of disorder present in the samples. We have calculated the diffuse intensity (D), from the relation $D = 1 - R - T$, from measurements with normally incident white light in the low energy regime ($a/\lambda < 1$, where a is the lattice parameter and λ is the wavelength of light in vacuum) for a certain crystallographic direction (normal to the surface of the samples). A high amount of imperfections in the unit cell such as vacancies, lattice displacements or stacking faults or the absence of a lattice produce diffuse light scattering which is here the only responsible for a decreased transmission and reflection, since PS absorbance[34] for the considered frequencies is negligible.
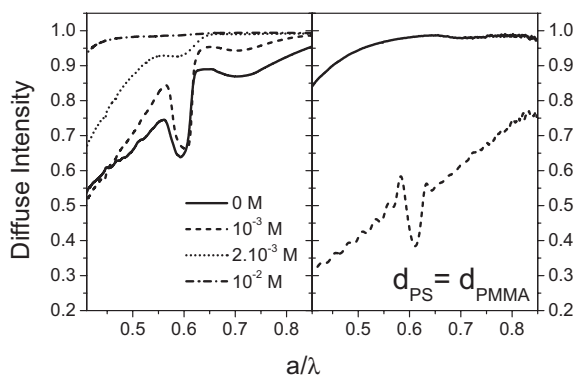

Figure 2. Left panel: plot of diffuse intensity measured in different samples as a function of the salt (electrolyte) concentration in the initial colloidal suspension. Photonic features, as the main gap, remain till the concentration of salt is enough to force the spheres flocculation thus preventing them from self-assembling. Right panel: diffuse intensity in the case of PS and PMMA spheres with the same diameter before (solid line) and after (dashed line) dissolution. Notice the presence of the gap before removal of PS spheres.

A perfect defect-free ideal colloidal photonic crystal will have $D = 0$. Even in the best case, a very high quality real opal does not present 100 % reflectance (0 % transmittance) for the frequencies inside the bandgap. On the contrary, a completely disordered system, randomly arranged, should present $D = 1$. A high value for D is a strong indication of disorder, while a decrease of D near the PBG is a sign of residual order. Thus, even apparently (by SEM inspection) very disordered samples were discarded after detecting a decrease in D in the regions of the PBG. Figure 2 shows D as a function of the reduced frequency for the two different systems grown, that is, a photonic glass (left panel) and a vacancy doped photonic crystal (right panel). Left panel of Figure 2 plots D for four different samples with a different $CaCl_2$ concentration (which is the concentration of ions in the charged colloidal suspension). According to the figure, an increasing of charge concentration in the colloidal suspension gives rise to an enhancement of D. The dip present at $a/\lambda \approx 0.6$ corresponds to the pseudogap taking place along the GL direction.[32] It is particularly remarkable how the dip associated with the pseudogap disappears upon increasing the charge concentration. A concentration 10^{-3} M is not enough to sufficiently attenuate the electrostatic barrier and the sample still shows traces of order. The presence of photonic crystal marks can be explained attending to the fact that such a low concentration of salt in the sample is not enough to force the flocculation of the spheres, which are still allowed to self-assemble in the evaporation process. Nevertheless, a concentration higher than 10^{-2} M is enough to force the spheres to agglomerate preventing the spheres from self-assembling. This is in agreement with the theoretical calculations[30] and confirmed by the experimental measurement of D.

The optical response of vacancy doped photonic crystals is shown in the right panel of the Figure 2. The dotted line represents D from the initial alloy PS-PMMA colloidal crystal
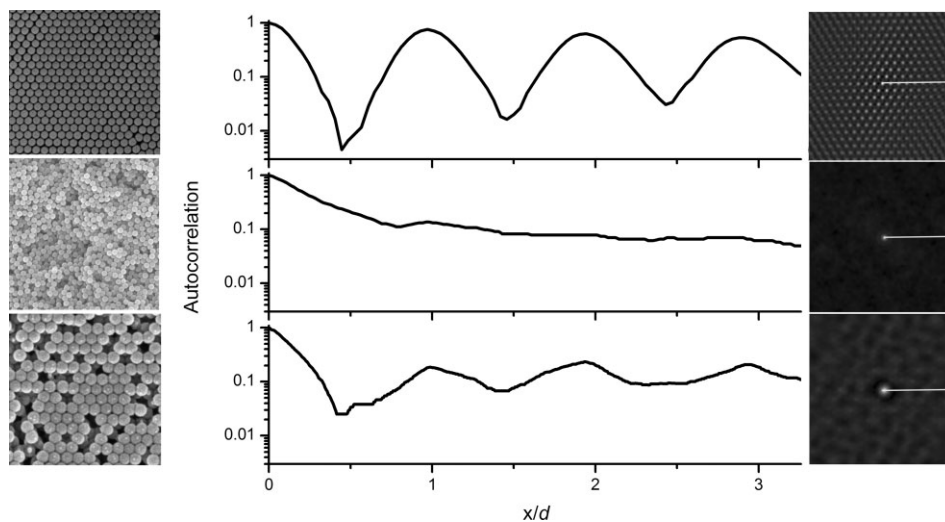

Figure 3. Left panel: SEM images of a opal-based photonic crystal, a photonic glass and a vacancy-doped photonic crystal. Right panel: Autocorrelation function of the surface SEM images from the three different systems. A plot profile of a cut in the autocorrelation function shows the order degree of each sample.

while the solid line represents the sample after PS removal. In the particular case that PS and PMMA spheres have the same diameter, an interesting system can be obtained. The selective dissolution of PS spheres in an alloy colloidal crystal can be optically followed. Before etching, D presents the usual features for a finite opal such as the monotonic increase for frequencies outside the gap, an enhancement in the low energy edge and an inhibition of frequencies inside the gap.[32] The transition between order and disorder is performed by removing the PS spheres and it is highlighted by the enhancement of D for all frequencies and, of course, by the disappearance of the photonic gap. The higher the relative concentration of PS, the more abrupt the transition is. An ordered opal can be doped with a very few and controlled amount of vacancies just reducing the relative concentration of PS spheres in the original binary colloidal suspension.

In order to obtain an independent measure of the ordering of our system, we have analyzed the autocorrelation function, $F(\tau)$, from SEM images and compared with the same function from an ordered sample (Fig. 3). The autocorrelation function describes the correlation of the contrast function $c(\mathbf{r})$, and gives a measure of the translational symmetry in the system:

$$F(\tau) = \int\limits_{-\infty}^{+\infty} c(\vec{r}) * c(\vec{r} + \tau) d\vec{r} \qquad (1)$$

If the particles are arranged with a frequent distance between first neighbours (that is, a certain local order) the function presents a maximum at the corresponding distance. Accordingly, the autocorrelation function of a random and isotropic arrangement of monodisperse objects, i.e., without positional correlation, is a delta function in the case of point-like objects or a decaying function if the objects have a size. The left panel in Figure 3 shows a comparison of SEM images of the three different systems and on the right panel a normalized plot profile of $F(\tau)$ from the corresponding system. The autocorrelation function from an ordered structure presents a periodic distribution of maxima due to its long range correlation (translational symmetry). The autocorrelation function of an infinite image composed by point-like objects randomly arranged is a Dirac-delta function. In our case, however, the repeated units are finite and the autocorrelation acquires a width. In addition, since every sphere is touching at least one other sphere, it becomes highly probable to find a high correlation one diameter away from each sphere. Therefore that, but only that, is a distance which has an enhanced correlation intensity. In the case of a photonic glass, $F(\tau)$ presents clearly a decaying intensity as a mark of the randomness of the sphere distribution. In addition, at the position corresponding to the nearest neighbour distance ($x/d = 1$), a small hint of a peak appears as a sign that no sphere can stand in air without being attached at least to one other sphere. On the contrary, $F(\tau)$ from a vacancy doped photonic crystal, which optically responds as a random system, presents attenuated periodic peaks typical of an underling order. Notice the dynamic range of the autocorrelation functions also giving a measure of the

relative order in the three structures. It is interesting to analyze the kind of disorder of the lattice with vacancies. For any given site the presence or absence of a neighbouring sphere is random (due to the synthesis method) but at the same time, the position of such a sphere (at a lattice parameter distance) is not random but precisely determined by the underlying lattice: it is a periodic lattice with random occupancy. Accordingly, a vacancy doped photonic crystal presents a correlated disorder. The comparison of optical spectroscopic analysis with the autocorrelation function analysis highlights now how, a high value of D (such as presented by a vacancy doped photonic crystal) does not ensure a fully random distribution of the system. On the contrary, an autocorrelation function analysis alone gives only information from the analyzed surface. Both analysis methods together are complementary to determine the degree of disorder of our samples.

Once the system is presented and its degree of disorder is analyzed we go a step beyond in functionalizing it. One of the most promising phenomena which could take place in a system such as a photonic glass is random lasing. Recently, laser emission has been shown to benefit from the high Q-value of the Mie resonances of a single sphere,[23] or a collective particle resonance[35]; microlasers based on random systems have also strongly attracted the attention of the photonics community.[36] To replicate that macroscopically in a photonic glass it is necessary to introduce optical gain. We have used a photonic glass as a template to infill higher refractive index and active materials. Among those, ZnO appears to be a very interesting one due to its remarkable properties as a conductor transparent in the visible range of the spectrum. Recently, high quality ZnO inverted opals grown by chemical vapor deposition (CVD)[37] have been reported. Furthermore, the relatively high ZnO refractive index provides enough dielectric contrast to improve the effect of disorder system on light propagation. For all these reasons, among the possibility of spontaneous light emission at room temperature, ZnO infiltration of the sample was carried out. If the PS spheres are then calcinated, ZnO random distributed shells are obtained (Fig. 4a). The inset of the Figure 4a shows cracked ZnO shells in detail. If the cycles in the CVD process are long enough (typically few minutes bubbling H_2O) the sample can be totally infilled by ZnO, obtaining a random distribution of air spheres in ZnO (Fig. 4b).

In conclusion, we present the realization of photonic glasses, solid random distributions of monodisperse spheres, which are a new photonic material. Two different growth methods have been explained. The first one based on the colloidal charge interaction, provides very thick and completely random samples which can be also used as templates to grow higher refractive index materials such as ZnO or Si. These samples can be a perfect playground to investigate light propagation in resonant random media, random laser and Anderson localization. The second method, based on binary colloidal suspension and selective etching, provides disordered thin films made by vertical deposition. This method can also be used for controlled vacancy doping colloidal photonic crystals,
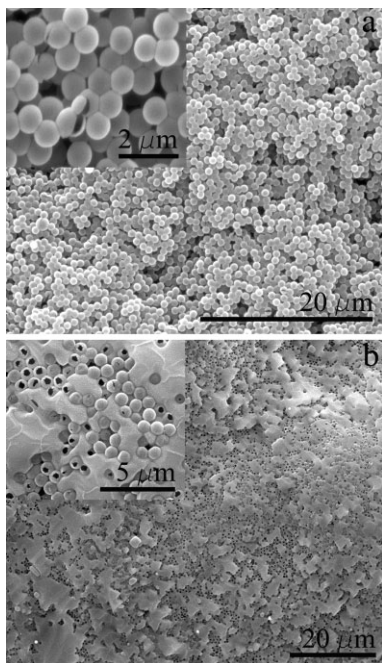
Figure 4. SEM images from disordered samples. a) ZnO disordered shells embedded in air. b) Air disordered spheres embedded in ZnO.

which can be a perfect model for investigation of the role of disordered in periodic photonic lattices.

Experimental

PS spheres are synthesized by free emulsion polymeration [38] with different diameters (780 nm, 457 nm, and 260 nm) with a polydispersity of 3 % measured with transmission electron microscopy. Colloids of 260 nm PMMA spheres were synthesized also via emulsion polymerization [39] with the same polydispersity.

Fourier transform infrared spectrometer (FTIR) was used to perform reflection and transmission spectra with normally incident white light in the visible and near infrared spectra. Microscope attached to the FTIR with an ×4 objective with a 0.1 numerical aperture was used to collect the light (corresponding to $a \pm 5.7°$ angular aperture). Optical spectroscopy and SEM were used to characterize the samples.

PS spheres used in this work have a surface potential –39.8 mV measured with the electrophoretic mobility of the spheres. In order to prepare the charged colloidal suspension 0.01 M a volume of an aqueous suspension of $CaCl_2$ (so $Z_1 = 2$) must be added to the initial polymeric colloidal suspension. The final suspension is shaked under ultrasound for 5 min in order to force the flocculation of the spheres. To grow the sample in a clean and hydrophilic microscope glass slide, a known area is confined by placing adhesive tape of a known thickness (on the order of millimetres). A volume of the charged colloidal suspension is then placed in the confined area at 50 °C for 3 h to evaporate the water. The thickness of the final dried sample depends on the volume and the concentration of polymer spheres in the charged suspension. Typically, we deposit 2 ml of a charged colloidal suspension with a concentration 2 % in a confined an area of 625 mm² obtaining a thickness of 140 μm. The filling fraction of the samples can be estimated as 0.5.

To obtain random distributions of ZnO shells in air ZnO was infiltrated in the samples with a modified CVD method [37] using a metal-organic precursor (Diethyl zinc 1.0 M solution in hexane from Al-

drich) which allows a fine control of shell thickness (less than 8 nm per cycle). The sample was heated for 32 h at 92 °C in order to dry it avoiding the melting point of the polymer backbone. At this point the samples were calcinated for 24 h at 450 °C reached through a ramp of 1 °C min⁻¹ in order to remove PS spheres and to obtain inverted ZnO shells.

Two kinds of colloidal suspensions were composed. The first was composed by 20 wt %. of 457 nm diameter PS spheres and 80 % 260 nm PMMA spheres. The second kind of colloidal suspension was composed by PS and PMMA with the same diameter 260 nm varying the relative concentration of each from 0 to 100 %. The opals were then grown using a modified version of the vertical deposition method [27]. A step motor (Oriel Stepper-18515) was used to vertically pull a hydrophilic glass microscope slide from the binary colloid. A fine control over the pulling velocity (0.2 μm min⁻¹) was exerted until the sample was completely removed from the colloidal suspension. PS selective removal was performed by immersing the samples in 99 % pure cyclohexane for 4 h.

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