

Self-Assembled Photonic Structures

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Photonic crystals have proven their potential and are nowadays a familiar concept. They have been approached from many scientific and technological flanks. Among the many techniques devised to implement this technology self-assembly has always been one of great popularity surely due to its ease of access and the richness of results offered. Self-assembly is also probably the approach entailing more materials aspects owing to the fact that they lend themselves to be fabricated by a great many, very different methods on a vast variety of materials and to multiple purposes. To these well-known material systems a new sibling has been born (photonic glass) expanding the paradigm of optical materials inspired by solid state physics crystal concept. It is expected that they may become an important player in the near future not only because they complement the properties of photonic crystals but because they entice the researchers' curiosity. In this review a panorama is presented of the state of the art in this field with the view to serve a broad community concerned with materials aspects of photonic structures and more so those interested in self-assembly.

1. Introduction

Self-assembled structures are pervasive in many areas of science and technology. And so are they specifically in the area of photonics. While it is arguable that they might compete in technological areas of modern photonics (owing to the lack of control they allow on structure detail of the devices possible) it is undeniable that, due to the nature of their synthesis, they are unbeatable in terms of cost. This has probably been behind the great attention these systems have received for more than twenty years and continue to receive nowadays. They have permitted to test many of the properties of photonic crystals (PCs) and will do the same with nascent photonic glasses.

While they are restricted to structures that *acquiesce* to grow by themselves from the building blocks that *lend* themselves to be synthesized, the imagination of researchers across the World has proven so powerful that a great many techniques have been

implemented and, as a result, many different structures were made possible.

In the last few years a numbers of reviews have appeared dealing with PCs. Some centre on selfassembly, some on other fabrication technologies such as various lithographies, others centre mainly on applications (such as lasers) but a general, comprehensive treatment of the subject of selfassembled photonic structures was lacking. In the following a glance is cast over the near past to gather the most significant findings and relevant results in or around the topic of self assembled photonic structures. There are many facets to the problem and we have sectioned the review accordingly. Even though the focus is placed on materials science aspects a careful watch is maintained on some fundamental optics and photonics aspects.

We devote special attention to the building blocks and assembly techniques (Sections 2 and 3). The processing of the structures is concerned with various issues but we chose to concentrate on infiltration chiefly because it is a very broad subject with many ramifications and results (Section 4). The propagation of light in these structures gives rise to the concept of Photonic Band Gap (PBG) which is the essence of their functionality and is treated in a section of its own (Section 5). This, however, is done putting the attention not so much on band structure of PCs but also on emission within these structures.

In a separate section, the problem of light transmission in disordered photonic structures is introduced (Section 6). Disorder has been beheld in this area as an unavoidable evil and techniques have been used in an attempt to minimize it. On the other hand, research conducted in the area of complex systems has paid little attention or completely disregarded the area of PCs. Thus the frontier area of photonic glasses where both disorder and regularity cohabit is very scarcely explored. For this reason we deemed a more in depth treatment was deserved.

An indispensable requirement of a compilation of this nature is a summary of applications (Section 7) that, although centred on optical applications considers other collateral applications too.

Rather than addressing the expert we aimed at those curious about the field or initiating in it. We intend to save them time in researching what has been already done and allowing them to choose a niche where their interest may fit. Thus in trying to make a helpful and didactic compilation it revealed natural to make an attempt at comprehensiveness and this requires a section devoted to numerical methods. In Section 8 we attempt to

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DOI: 10.1002/adma.201000356

avoid a very deep theoretical description on the methods and we concentrated on providing a guide to those in need of a means to model their results. The aim is providing a catalogue of available numerical tools and when to use each.

2. Building Blocks

Self-assembly refers to the process in virtue of which order or structuration is attained without direct external action (typically referring to human intervention) and may occur in many different systems at different scales:^[1] from angstrom size elements (atoms forming a crystal) to planets gravitationally arranged in solar systems. Nature is copious in these phenomena and Science has always wished to learn how it really works. It is of paramount importance to deepen the knowledge about a self-organized systems and processes found in nature not only from a technological point of view but to satisfy natural human curiosity too. But sometimes it is sufficient to know how to control them, making predictions to design new “natural” systems in our laboratory.

Being more specific, self-assembled materials are getting much attraction lately, especially at the nanoscale.^[2] The reason for this is the fact that exerting control at nanometre scale is only possible through very sophisticated techniques that most often require very expensive means. Nanostructured materials are hard to realize and self-organization usually offers systems where the structure arises from this natural process. A speed factor must also be considered since a full bottom-up control is usually sequential and, while for prototyping might be viable, has serious shortcomings for 3D structures.

Material scientists have been enthusiastically involved in the field of ordered photonics like PCs,^[3,4] which has steadily increased in the past twenty years with novel material techniques for accurate optical performances. Typically self-assembly is governed by thermodynamic processes that occur when the system is let to explore its phase space. As far as this review is concerned self-assembly takes place in a colloidal suspension when the particles forming the colloid move in a Brownian fashion subject to the constraints particular to the system at hand which are often used to “stimulate” the system to assemble as best suits the application for which it is meant.

Photonic self-assembled structures essentially comprise PCs and glasses.^[5] These are composed of assemblies of identical shape and size elements crystallized under different lattices. Obviously the first requirement to make good self-assembled photonic structures is the monodispersity in size of the building blocks that make them up.

There are many chemical methods that produce compounds in the shape of solid powders or, in general, as finely divided material. Many materials can be synthesized as particles uniform in size and shape.^[6,7] But probably the monodisperse particles most extensively used when an orderly assembly is required are the spherical ones.^[8] Their interactions are more isotropic and stacking is easier. Since different materials require different synthesis techniques and offer different functionalities and processing possibilities a large number of them have been investigated. This includes organic and inorganic materials, and among them insulators, metals and semiconductors. As far as



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morphology is concerned the spherical shape is dominant but others have been explored too. Even restricting the survey to the spherical shape it is possible to find different approaches such as homogeneous particles or composite particles and among them so called Janus and core-shell.

Next, brief reports on various aspects of fine particles synthesis for photonic applications are collected.

2.1. Organic Spheres

Among the materials used for opal^[9] – faced centred cubic (fcc) arrangement of monodisperse microspheres – assembly the widest spread are polymers, mainly polystyrene (PS) and poly(methyl methacrylate) (PMMA). For the preparation of these beads there are a host of techniques^[10] all under the umbrella of polymerization but with different approaches such as precipitation polymerization,^[11] emulsion polymerization,^[12] dispersion polymerization,^[13] seeded polymerization,^[14] inversion emulsification,^[15] swelling polymerization, suspension polymerization,^[16] and modifications on them.

Included in the organic particles group, the microgel family of spheres is very attractive for photonic applications. A microgel particle is a cross-linked polymer particle which is swollen by an appropriate solvent.^[17] Staudinger and Husemann were the first to prepare microgel particles.^[18] They polymerized divinylbenzene (DVB) at high dilution in an appropriate solvent to achieve swollen cross-linked polymer particles. Poly(N-isopropylacrylamide) (PNIPAM) is the most studied water-swellaible microgel system.^[19] Water behaves as an appropriate solvent through hydrogen bonding with the amide groups at room temperature. This hydrogen bonding with water is increasingly disrupted on heating causing water to act as a poorer solvent leading to gradual chain collapse. This thermosensitive polymer

has a volume phase transition at ~ 32 °C, such that the particle size decreases at high temperatures. Thermal annealing of concentrated solutions of PNIPAM particles allows for particle self-assembly as the particles return to their swollen state. This procedure provides a convenient method for rapid fabrication of crystalline materials, and the soft particle construct additionally enables simple adjustment of optical properties by varying the polymer volume fractions.^[20]

As a last example of organic spheres it is worth mentioning the monodisperse carbon spheres.^[21] In a size range of 150–1500 nm these particles can be synthesized from glucose under hydrothermal conditions. The synthesis involves non-organic solvents, initiators, or surfactants. This ensures that the as-prepared particles are non-toxic enabling their use in biochemistry or bio-diagnostics.

2.2. Inorganic Spheres

Although, the organic spheres have demonstrated a high versatility for many applications, highly inert materials are necessary (both chemically and thermally). For this motive inorganic compounds are best suited. Typically inorganic compounds withstand higher temperatures and have chemical properties very different from those of organic ones. Among them SiO_2 has acquired supremacy but is not the only material of interest.

2.2.1. Oxides

The best known method for monodisperse SiO_2 spheres was originally developed by Stöber *et al.*^[22] and relies on the hydrolysis of a silicon alkoxide and posterior condensation of alcohol and water to form siloxane groups. Because of their chemical structure, these beads present a surface charge, which is screened by the ions in the medium. Under appropriate conditions of temperature, pH, and concentrations this synthesis process yields spheres with diameters ranging from a few nanometres to a few micrometres. Although the reason why is still controversial, very monodisperse colloids (a few percent standard deviation in diameter) can be obtained for sizes between 200 and 600 nm (Figure 1a). For larger sizes a strategy based on the growth in the presence of small seeds has proven successful.^[23] Everything seems to indicate that the final size of the produced particles responds to a correct balance between the nucleation process (by which new particles are created) and that of aggregation (through which those particles grow at the expense of available monomers). For that reason, the concentration of seeds in a re-growth process must correctly match the reaction condition in order that no nucleation occurs while an optimum use of the SiO_2 precursor is made.

Higher refractive index monodisperse spheres have as well been generated by hydrolysis of metal alkoxides in alcohol solution.^[24] Barringer *et al.* reported the use of this method to prepare monodisperse TiO_2 spheres.^[25] This method showed the difficulty to avoid the formation of aggregates. Some modifications were necessary to control the colloidal stability improving the quality of the samples. One method consisted of increasing the charge of the particle surface by adding a salt.^[26] Other way to increase the colloids stability is based on the steric stabilization

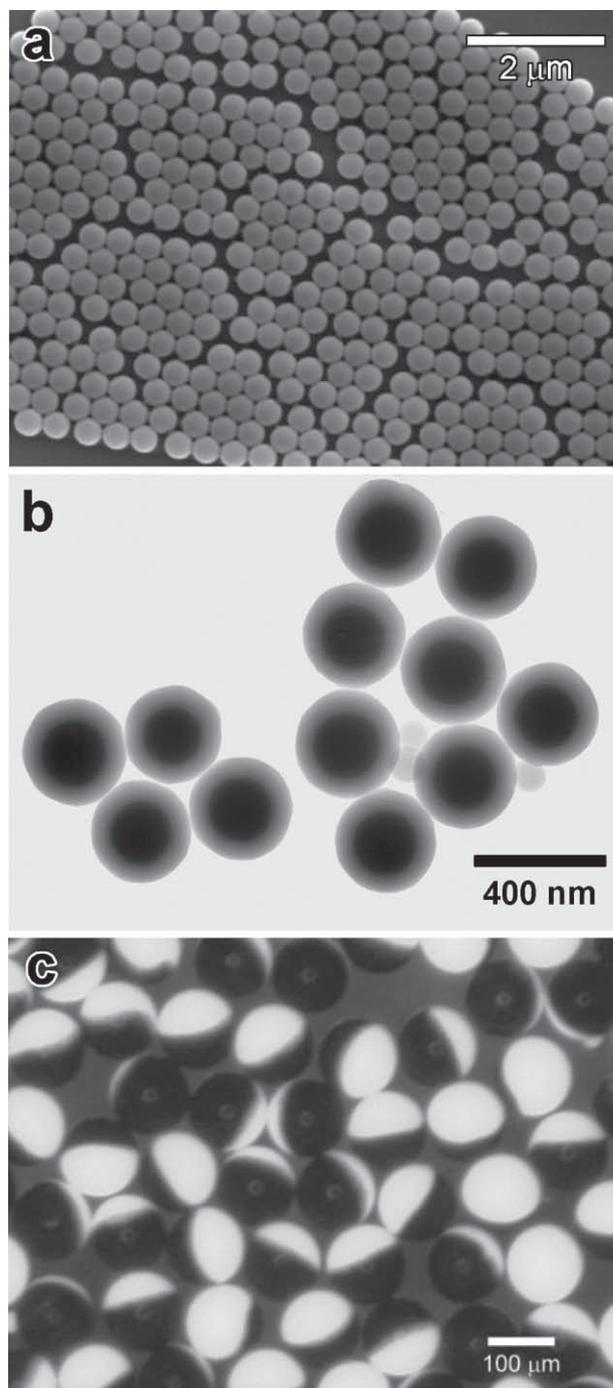


Figure 1. Electron microscopy images of (a) SiO_2 , (b) Pb@SiO_2 (adapted from Ref. [55]) and (c) bicolored polymeric (adapted from Ref. [87]) spheres.

of the particles. Jean and Ring used hydroxypropylcellulose, to control the size and monodispersity of the colloids.^[27] Some further modifications are studied to prepare highly monodisperse TiO_2 spheres to fabricate PCs.^[28]

Other material with interesting properties for photonic applications is ZnO . This material has a high refractive index and it is an efficient emitter in the near UV ($\lambda = 385$ nm), exhibiting

lasing behaviour. ZnO can be prepared as monodisperse spheres by polyol method.^[29] Polyols are adequate solvents to prepare inorganic compounds via precipitation from a liquid phase. Their high dielectric constants allow them to dissolve inorganic compounds and their relatively high boiling points offer a wide operating-temperature range for preparing inorganic compounds. In this method heating salts in polyalcohols, which act as solvents as well as reducing agents and stabilizers, leads to the formation of fine particles. By modification of the Jezequel method, Seelig *et al.* obtained ZnO spheres uniform enough to fabricate PCs.^[30]

The polyol method has also been used to synthesize dispersions of different metals by reduction,^[31] and other oxides as CeO₂.^[32]

Other Lanthanoids oxides have been made by thermal decomposition via homogeneous precipitation in the presence of urea.^[33,34] The synthesis of monodisperse lanthanide compound^[35,36] have been extensively studied because of their interesting optical, magnetic, electrical, and catalytic properties and their wide applications in various aspects of contemporary science and technology.^[37] Homogeneous precipitation by urea is a relatively simple, reproducible, and economically feasible method for its potential large scale production.

2.2.2. Chalcogenides

In very much the same way as some oxides mentioned before, monodisperse spherical metal sulphides can be prepared by thermal decomposition when the urea is exchanged by thioacetamide.^[38,39] In this method, like that of Chiu,^[40] consisting in passing hydrogen sulfide through a Zn-EDTA (Ethylenediaminetetraacetic acid) aqueous solutions, the quantities of resulting particles is small due to dilute starting solutions. The advantage of thermal decomposition method is that it allows a broader range of sizes. By using this method, monodisperse spherical ZnS particles from 100 nm to several micrometres can be produced with minimal surface roughness.^[38]

PCs from polyelectrolyte-stabilized ZnS spheres have been fabricated by convective method.^[41] This material is optically interesting because of its high refractive index ($n = 2.36$ at $\lambda = 589$ nm) and low absorption at visible wavelengths.

CdS monodisperse spheres can also be made by thermal decomposition covering a range from 0.1 to 1 micrometre. The size of the resulting spheres depends on the concentration of thioacetamide and on the length of the reaction. The estimated refractive index of these particles was 1.92 at $\lambda = 546$ nm.^[39]

The solvothermal method also allows to make CdS monodisperse spheres. In this method, the size of uniform CdS particles can be tuned continuously from the nanometre to the submicrometre scale by varying the reaction conditions. A higher amount of CdS particles is obtained from this method, which it is more convenient for practical applications. These high concentrated suspensions allow to fabricate PCs by spin coating.^[42]

Both ZnS as CdS can also be synthesized by gel-sol process.^[43,44] In this process a Metal-EDTA complex in the presence of gelatine reacts with thioacetamide to make monodisperse metal sulphides spheres.

ZnSe is also an important semiconductor for photonic applications due to its high refractive index, transparency in

the visible region and blue emission.^[45] It is used to form II–VI light-emitting diodes and diode lasers.^[46] Monodisperse ZnSe spheres have been prepared by controllable in-situ aggregation of ZnSe nanoparticles which were produced via a simple hot-injection route.^[47] The particle size can be tuned between 100 and 800 nm with a size distributions less than 6% broad.

2.2.3. Metals

Ever since Moroz showed the rich properties of fcc structures of metal or metallodielectric spheres,^[48] the interest in this kind of particles has increased in the PCs field. Although different methods are known to make metal nanoparticles,^[49] just a few works describe the synthesis of metal particles with diameters bigger than 100 nm. Large gold^[50] and silver^[51] spheres with relatively narrow size distribution have been prepared by reduction of metallic ions with ascorbic acid in presence of gum arabic as steric stabilizer. The proposed mechanism involves the aggregation of nanometric particles formed after the nucleation process. The particles size can be tuned between hundreds of nanometres and several micrometres depending on the experimental conditions.^[52] Using hydrazine as reducing agent palladium spheres can be synthesized from Pd-urea adduct spheres previously obtained by reduction of palladium ions with urea at temperatures around 80 °C.^[50]

Trying to narrow the size distribution of the spheres Xu *et al.* prepared several submicrometer metal and semi-metals (Au, Pb, Bi, Sb, and Te) particles using inverse opal structures (fcc arrays of air spheres in a high refractive index host) as templates.^[53] They used two different approaches; Gold was grown by electrochemical deposition inside the matrix and the other elements, which have low melting point, were infilled by a melt process. They also prepared several thermoelectric alloys (Bi-Sb, Bi-Te, and Bi-Te-Se). This method is quite complex involving many steps to get metallic spheres. The solution-based methods show some advantage with respect to the template approach. The synthetic procedure is simpler and the amount of produced colloidal particles is higher. Two solution-based approaches describe the synthesis of monodisperse submicrometer spheres of low melting point metals.^[54] In the first approach, metal acetates are thermally decomposed in the presence of Poly(vinyl pyrrolidone) as stabilizer during the reflux in polyols. The high boiling point of the used solvents and the low melting point of the metals allow having liquid droplets in the solvent. An abrupt fall of temperature does the particles obtained keep the spherical shape of the droplets in the solvent. With this approach Bi and Pb spheres were obtained in ethylene glycol and tetra(ethylene glycol) respectively. In the second approach metallic powders are directly added to boiling solvents and melted to produce drops in presence of Poly(vinyl pyrrolidone). A fast cooling allows to obtain Bi, In and Cd/Pb alloyed spheres in di(ethylene glycol), dodecane and tetra(ethylene glycol) respectively.

Both procedures generate submicrometre spheres with a size distribution below 5% and smooth surfaces. The quality of these particles allow to fabricate metallodielectric PCs by self-assembly.^[55]

2.3. Core-Shell Spheres

Synthesis of core@shell particles is a successful method to fabricate novel materials with different compositions and morphologies, as it is not possible to synthesize the materials in desired morphologies.^[56] These particles are synthesized for several applications such as photonics,^[57] catalysis,^[58] sensing,^[59] therapy,^[60] etc.

Core@shell structures can be prepared using all kind of materials, semiconductor, metals and dielectrics in different combinations as insulator@insulator,^[61] insulator@semiconductor,^[62] insulator@metal,^[63] semiconductor@insulator,^[64] semiconductor@semiconductor,^[65] semiconductor@metal,^[66] metal@insulator,^[65] metal@metal,^[67] and in a multishell structure.^[68]

Several methods have been used to synthesize core-shell particles in the micrometre range, some of which are described below.^[69]

In the layer-by-layer (LbL) process charged species of opposite charge are adsorbed onto the particle surface. The thickness of the coating is tuned by the alternate adsorption of oppositely charged species. This versatile method allows to deposit polymer, lipid, proteins etc.^[56]

Other method frequently employed for its simplicity and ease of control on the shell thickness is the sol-gel approach. SiO₂ coatings have been prepared onto metals (Figure 1b),^[55] semiconductors,^[64] insulator,^[56] and magnetic^[70] particles by this method. The particles are coated with SiO₂ by base catalyzed hydrolysis and condensation of a silicon alcoxide in an alcoholic medium.^[22] By sol-gel method coatings of TiO₂,^[71] zirconia,^[72] tantalum,^[73] Gadolinium oxide^[74] and Gd₂Ti₂O₇ doped with Europium ions^[75] have been achieved.

The chemical conversion method allows the direct preparation of core-shell and hollow semiconductor spheres. By using active material spheres as reactant and template it is possible to make a series of other semiconductors. From ZnSe hollow spheres it is possible to prepare hollow and core-shell spheres of more stable chalcogenides (CdSe, Ag₂Se, CuSe) sulphides and oxides.^[76] The chalcogenide core-shell particles can also be prepared from amorphous selenium. The reaction of selenium spheres with silver atoms forms Se@Ag₂Se spheres. Opals made with these particles show thermally switchable stop bands due to the phase transition of Ag₂Se around 133 °C (from β to α).^[65] Se@CdSe, Se@ZnSe and Se@PbSe spheres are obtained from Se@Ag₂Se via cation exchange. These particles show a superparamagnetic behaviour when magnetite nanoparticles are incorporated into the selenium core.^[77,78] Starting from lead particles, Pb@PbS and Pb@Ag have been prepared by reaction with sulphur vapour or silver ions in an aqueous solution, respectively.^[67]

By the surface-layer-absorption templating technique it is possible to obtain monodisperse Ga₂O₃ and GaN hollow spheres.^[79] Gallium ions are adsorbed onto the surface layer of carbon spheres whose surfaces are hydrophilic.^[21] A later calcination process forms Ga₂O₃ hollow spheres, which are converted into GaN in an ammonia atmosphere at around 800 °C. These particles show more complex photoluminescent behaviour than the GaN nanoparticles.

Metallic shells have been grown on modified SiO₂ spheres decorated with gold nanoparticles (1–2 nm) by reduction of chloroauric acid^[63] or silver nitrate.^[80]

A particular case of core@shell structure are the hollow spheres.^[81] These particles can be synthesized by a one-step self-templated method in which large precipitates grow at the expense of smaller precipitates caused by energetic factors. This method has been used to synthesize hollow structures of a wide range of materials.^[82,83] Although in many cases hollow spheres are fabricated by coating a sacrificial template with a shell of desired materials and subsequently removing it via selective etching with a solvent, an acid or calcination in air.^[69] The most common sacrificial templates used are SiO₂ and polymer spheres but resin spheres, vesicles have also been used as templates. With this method it is possible to prepare insulator, semiconductor and metal hollow spheres.^[81]

2.4. Non Spherical Symmetry

It is well known that fcc lattices of spherical scatterers do not produce full PBGs. And it is well known too that spherical colloidal particles crystallize in fcc lattices. These two facts triggered the synthesis of particles with non spherical symmetry. They come mostly in two flavours: particles with spherical shape but anisotropic chemical character (known as Janus particles) and particles with non spherical shape (mostly dimmers, trimers etc).

P.G. de Gennes was one of the first scientists to use the term Janus for the description of particles whose surfaces of both hemispheres are different from a chemical point of view.^[84] The name was taken from the roman deity Janus usually represented with two faces (placed back to back) head. By considering Janus grains displaying simultaneously polar and apolar faces, De Gennes described their spontaneous monolayer arrangement for instance at air/water interface.^[85,86]

These particles can have diverse functions because of their anisotropic nature. An example is two-colored beads of diameter 30–150 μ m, having both electrical and colour anisotropy (Figure 1c).^[87] Other such particles that have been proposed include amphiphilic spheres analogous to surfactant molecules,^[85] pH-sensitive particles,^[88] and colloidal particles having a dipolar charge distribution.^[89] The electrohydrodynamic jetting has allowed to obtain Janus particles at the submicrometre range.^[90]

Nowadays, Janus particles are considered to comprise, not only those with chemical anisotropy but also with asymmetry related to physical properties or their shape.^[91]

The particles with non spherical geometric open the possibility to get packing structures with lower filling fraction in contrast to the spherical particles which tend to crystallize in high density packing. In the vast majority of cases, they adopt an fcc structure and in the case of highly charged colloids body centred cubic structures. Theoretical calculations show that this kind of structures does not show a full PBG. However the diamond structure can present a wide PBG between the 2nd and 3rd bands, opening for a relatively low refractive index contrasts.^[92] This thermodynamically unstable structure cannot be obtained by self assembly from spherical colloids essentially due to its low filling fraction. A new class of diamond-type structure using colloidal cluster building blocks has been proposed.^[93] The array of colloidal tetrahedra shows a robust PBG for a low refractive

index contrast. For this reason the preparation of spheres clusters and nonspherical building blocks are of great interest for photonic applications. Stöber *et al.* in 1969, by using a special centrifuge, obtained polyhedral clusters of latex spheres from liquid droplets.^[94] They isolated dimeric, trimeric, tetrahedral, octahedral clusters as well big spherical aggregates. The use of liquid and emulsion droplets has been used by Velev *et al.* to create large aggregates with different morphologies.^[95] Pine and co-workers using also liquid emulsion droplets prepared clusters formed from 2 to 15 polystyrene spheres. The identical polyhedra for each number of spheres were separated by centrifugation in a density gradient.^[96] Both the use of oil-in-water emulsion^[97] and phase-inverted water-in-oil emulsion^[98] allow to prepare colloidal clusters from bidisperse colloids. Aerosol-assisted technology has also been satisfactorily used to make polyhedra monomodal and bimodal SiO₂ clusters as well as hollow SiO₂ microclusters.^[99] The pattern-assisted approach^[100] also allow to prepare homo^[101] and heteroclusters^[102] although the production yield is low.

In an effort to obtain more copious quantities of these colloids diverse techniques have been used to directly synthesize the nonspherical building blocks. Particle dimers of polymers, oxides, chalcogenides and metals have been prepared.

SiO₂ dimers have been formed from shear induced aggregation using ammonia and ethanol to cause destabilization in solution.^[103] Addition of tetraethylorthosilicate to a suspension of aged SiO₂ colloids has been tested too.^[104] A heat assisted convective assembly technique was used to produce ZnS dimers, trimers, and tetramers.^[105] Polystyrene dimers can be synthesized by salting out-quenching-fusing technique. The high ionic strength promotes colloid aggregation. After a rapid flocculation time, the colloid is quenched by mixing in a large quantity of deionized water to prevent further aggregation. Through heating above the glass transition temperature of the polymers, the dimers are fused together.

Through salting out-quenching gold and silver homodimers, and gold-silver heterodimers can be prepared.^[106] In these cases the high melting point of the metals does not allow to enhance the stability by fusing but the high Hamaker constants make the attractive van der Waals forces maintain the stability of the dimers. SiO₂-polymer heterodimers can be synthesized by this method,^[107] as well as by one-step reaction through a miniemulsion polymerization technique.^[108] The organic and inorganic reagents were confined in miniemulsion microreactor droplets. After the formation of polystyrene and SiO₂, internal phase separation inside the droplets was accelerated owing to the hydrophobicity of polystyrene and the hydrophilicity of SiO₂. Asymmetric dimers can be synthesized from polystyrene spheres by seeded emulsion polymerization, that is, a second lobe forms due to phase separation from a crosslinked seed.^[109] Monolayer films from polystyrene asymmetric dimer colloidal particles can be formed on a silicon substrate using a heat assisted vertical deposition technique. The confining effect of the meniscus height (see below) drove the formation of the resulting oblique and hexagonal lattices with controlled orientation.^[110] By a modified seeded-polymerization technique trimers and tetramers can be prepared in large-scale synthesis.^[111] The technique involves controlling the directionality of phase separations in the seeded-polymerization

technique by manipulating the crosslinking density gradients of the seed particles.

By a sol-gel process, mentioned previously, it is possible to make anisotropic particles as cubes, rods, ellipsoids and peanut-shaped hematite particles in relatively large quantities.^[112] The morphologies of the colloidal particles could be altered by increasing the concentration of the shape controller ions or using organic additives.^[113] Theoretical calculations show that the self-assembly of peanut-shaped ferric oxide particles in a fcc structure allows to create a PBG between the 2nd and 3rd bands.^[114] To create a full gap above the ferric oxide absorption ~500 nm submicrometric peanut-shaped particles have to be synthesized.^[115] Dense ordered monolayers of peanut-shaped hollow SiO₂ have been prepared under confinement. In this structure, particle lobes tile a triangular lattice while their orientations uniformly populate the three underlying crystalline directions.^[116]

Many other metal oxides, metal chalcogenides and metal can be made in non spherical shape in a micrometre and submicrometre scale.^[117] Some of these non spherical shapes (dimers, trimers and peanut shaped particles) are shown in **Figure 2**.

3. Self-Assembly

The process of self assembly of finely divided materials is often viewed only from the perspective of the arrangement into ordered structures like PCs. In this case the goal is optimizing the conditions to obtain a high quality crystal. Typically a large single crystal size is pursued, with controlled orientation, reachable in the shortest times and with good mechanical properties etc. Minimizing the residual disorder is a major goal. Obviously this is never fully eliminated and partial disorder is always present. However fully disordered structures are, on the other hand, interesting too (see below). In this case getting rid of remnant order is equally important and hardly fully attained. It can be immediately seen that the dichotomy order/disorder is pervasive. The methods to obtain either extreme are surprisingly similar though. **Figure 3** shows SEM images of completely ordered and completely disordered structures.

3.1. Ordered Structures

The process of self-organization of colloidal particles has been studied extensively for the last two decades.^[118] Seminal work from Pusey, Okubo and Nagayama dealt with this problem from different points of view. Okubo centred his studies in colloidal crystals (self-organization of colloidal microparticles in solution),^[119] Pusey studied glass transitions in three dimensional concentrated arrangements of colloidal particles^[120] whereas Nagayama centred his efforts in studying two dimensional systems (colloidal monolayers).^[121,122] On one hand this system is a handy model to study atomic crystals formation,^[123] defects,^[124] or mechanical properties,^[125] among others. On the other hand, 3D structures based on self-assembled colloidal beads (artificial opals) were firstly used by Astratov *et al.* in the mid nineties as a natural method to obtain 3D PCs in the optical range.^[126] If useful photonic structures based on self-assembly are to be

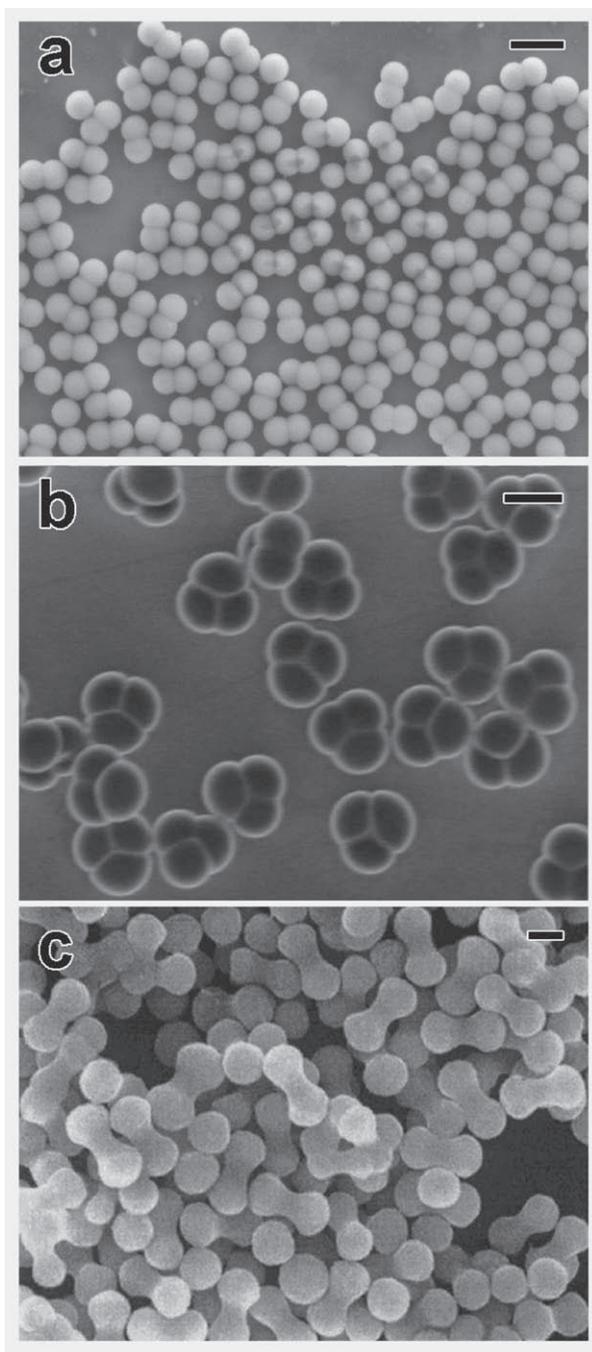


Figure 2. Scanning electron microscopy images of (a) SiO₂ dimers (adapted from Ref. [104]), (b) crosslinked PS triangle particles (adapted from Ref. [111]), (c) hematite peanut-shaped particles (adapted from Ref. [115]). Scale bars are 1 μm for a and c and 5 μm for b.

created it is essential to know how this process works. From colloidal crystals to monolayers, both from organic and inorganic beads have been considered and tested over the last few years. Here we will focus on the vertical deposition method which is, to date, the most widely used one to produce PC templates.

Several methods have been proposed to realize optimal 3D structures with PC properties, starting from SiO₂ or polymer (mainly PS or PMMA) spheres. The first method proposed

was natural sedimentation of SiO₂ spheres in diluted aqueous colloidal suspensions. After deposition, a posterior sintering process was necessary to increase mechanical stability, yielding high quality opals for diameters smaller than 400 nm.^[127]

Woodcock theoretically demonstrated that when hard spheres self-assemble in thermodynamical equilibrium, the fcc is slightly more stable than the hexagonal close packed one (hcp).^[128] This is well suited to the natural sedimentation method used in the early trials of self-assembling PCs. However, the same arrangement has been found in systems well separated from equilibrium (like those obtained by vertical convective deposition) suggesting a different mechanism.

Alternatives to the natural sedimentation method were proposed to deal with larger spheres (up to 1 micrometre) based on electrophoresis^[129] or confined environments^[130] where the effects of gravity were minimized improving crystallization quality. Here, the imposed geometry forces the spheres to accommodate to a given fixed thickness producing dislocation defects when this thickness is not commensurated with a high symmetry layering thickness.^[131]

The ultimate method proposed and nowadays most widely used is the vertical deposition or convective deposition method,^[132] which is based on the evaporation of the liquid (generally ethanol or water) forcing the spheres to arrange in the meniscus formed between a vertical substrate, the suspension and air. This method provides precise control over the thickness with superior crystalline quality of the structures even for diameters larger than 1 micrometre, if dealing with polymer beads. For large SiO₂ spheres there have been some improvements of this method but only working in a very narrow set of experimental parameters and, therefore, hard to implement successfully.^[133]

Recently, Norris *et al.* have discussed the effect that the solvent flow has on this process.^[134] Briefly, evaporation on the surface of the meniscus creates a current in the liquid that impels the spheres. Once some spheres are arranged, the spaces in between give rise to channels through which the liquid is flowed. Channels are different in different crystal directions which enhances the driving force for certain orientations. It is believed that seed crystallites with certain orientation capable of draining more efficiently succeed in determining the final orientation and ultimately giving rise to an fcc lattice.^[135] This configuration can be described by saying that it corresponds to an fcc lattice with its [111] axis perpendicular to the substrate and that its (111) planes (compact hexagonal arrangements) have one of their rows of spheres vertical (perpendicular rather than parallel to the meniscus).

Crystal thickness, starting from one layer, increases monotonically with time as solvent evaporates until an equilibrium thickness is reached. This thickness is determined by the meniscus properties which, in turn, depend on temperature, rate of evaporation (ambient humidity and vapour pressure), surface tension of the liquid and concentration of the colloid.

At the early stages of self-assembly when only a few layers have formed very recent work have studied the epitaxial growth of colloidal monolayers and the island formation, similar to those occurring in atomic epitaxy.^[136] Under these conditions it is also found experimentally that regions with mixed hcp, fcc and a mixture of both are created which are not easy to interpret

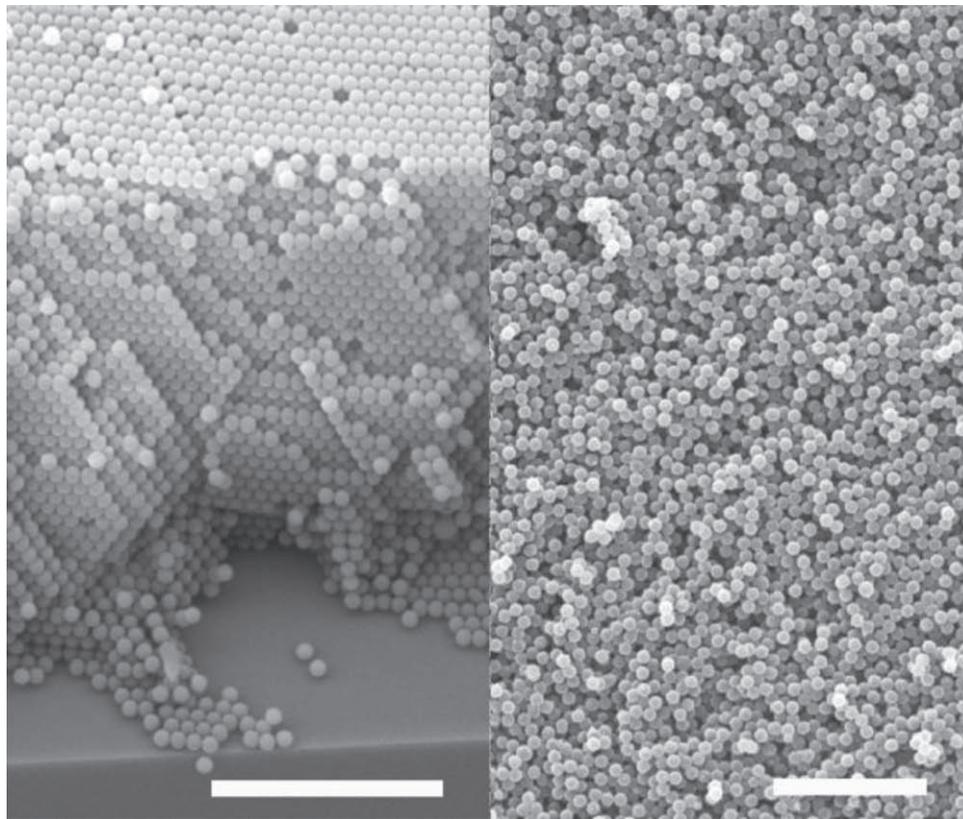


Figure 3. SEM image from a PC cleaved edge (left panel, scale bar is 10 μm). SEM image from a photonic glass surface (right panel, scale bar is 10 μm). Both samples are made of PS spheres (2% of polydispersity measured by transmission electron microscopy) and have centimetres squared areas and millimetres thickness.

but can be fully characterized optically.^[137] The presence of such stacking disorder has also been studied for bulk opals, where the optical response was seen to be modified with respect to the ideal sample.^[138] Oscillatory thicknesses can also be appreciated on those regimes of growth that can be attributed to temporal variations of the evaporation velocity caused by periodic changes of the friction force at the meniscus.^[139,140] The understanding of these phenomena is of paramount importance for optimal fabrication and further processing and it is yet far from being completely achieved. Recently, various attempts based on the vertical deposition method have dealt with improving crystal quality by modifying key parameters such as evaporation rate, pressure, temperature, etc. By applying negative pressure (vacuum) one can reduce the density of defects and, in particular, obtain large crack-free single crystal domains up to 1 mm^2 for polystyrene spheres of 300–400 nm.^[141]

A different route to control solvent evaporation, or growth rate, is to lift the substrate with a given velocity using a step-motor.^[142] This method is capable to produce also 2D arrangements or even binary colloidal crystals in a faster way when using confined environments.^[143,144]

A very recent improvement over these meniscus drawing methods has demonstrated huge (cm^2 size) single domain 2D arrangements of polystyrene spheres. The key parameter here is to maintain the meniscus curvature as low as possible during drying using a wedge-shaped cell.^[145]

Other alternatives are methods based on the Langmuir-Blodgett technique. Here, monolayers formed in the air/liquid interface^[146] can be transferred to a substrate, forming either 2D^[147] or even 3D^[148] patterns by layer-by-layer procedure, although the optical quality of the structures formed in this way might be improved. Some approaches have been taken in this direction reducing the abundance of cracks^[149] or using substrates with predefined motives^[150] to improve crystallization. Similarly, monolayers previously grown on flat substrates can be peeled off and be transferred to any other substrate^[151] or even curved surfaces.^[152] 3D structures can also be grown on the air/water interface and then transferred to a solid substrate after evaporation.^[153]

Recently, Jiang *et al.* have developed a new method to produce large-scale SiO_2 colloidal PCs by spin coating.^[154] This new procedure allows the growth of planar artificial opals on large surfaces (wafer size) in a rapid way (minutes' time). Here, the SiO_2 particles are on non-volatile solvents, which are photopolymerized after casting to provide mechanical stability. Selective etching of particles or polymer yields porous structures with PC properties. The extension of this method to deal with commonly used polymer beads has been recently developed by Míguez using volatile solvents controlling the final thickness of the structures from one to several monolayers in a very uniform way.^[155] Although the crystalline (optical) quality of these structures is lower than samples obtained by vertical deposition,

this technique offers other advantages in terms of fabrication, which might be important in future industrial mass production.

Shear-induced order in colloidal crystals has been studied since the last 20 years^[156] and some examples show how it is possible to switch between fcc and hcp arrangements by this means.^[157] Polymer embedded colloidal beads can be rendered into flexible opals,^[158] following similar procedures, or even prepared highly optimized dry colloidal crystals without cracks.^[159]

DNA directed self-assembly is a novel approach that can boost the possibilities of colloidal self-assembly. By using DNA one can basically pre-design the structure by choosing different combination of basis or chains, forcing the beads to organize following imposed geometries. Bianchangelo *et al.* have recently demonstrated the possibility of directing colloidal crystallization by means of DNA binding specificity,^[160,161] which can in fact be switched on and off by using temperature, adding versatility to this kind of novel structures.^[162]

This example serves us well to discuss one of the drawbacks found in colloidal self-assembly: the crystalline structure. Although the most favourable structure to develop a full PBG is the diamond lattice^[92,114] artificial opals tend to self-organize in fcc regardless of the method used. This can only be avoided by forcing the spheres to violate the minimum energy arrangement. Some work have addressed this problem experimentally building colloidal diamond structures by robot micromanipulation.^[163] One can also play with the substrate nature and force the colloid to organize following a pre-defined pattern^[164] forcing the growth into other directions different from the (111), the most common.^[165] For example, the growth on the (100) face is not common but can spontaneously appear on self-assembled structures^[166] which could be explained by commensurability issues at certain meniscus thicknesses^[131] or edge effects on the meniscus.^[167]

By combining beads of different sizes it is also possible to realize more complex crystal structures. Pusey's pioneering work studied the conditions to obtain stable binary mixtures of hard spheres^[168] similar to those found in natural opals^[169] or in charged stabilized colloidal suspensions.^[170] More recently, different approaches have been taken to control the growth of

binary structures by vertical deposition: In 2D, Kitaev *et al.* prepared patterns of binary colloids with optimal quality.^[171] However, extending this method to 3D, layer-by-layer growth of similar structures yielded far poorer crystal quality.^[172] The problem found here is that the solvent flow can provoke the jamming of the fluid channels by the smaller particles depending on the size ratio.^[173] A new method based on local infrared assisted evaporation^[174] has been recently developed to overcome these problems producing large-scale binary colloids assembly with higher quality.

Self-assembled diamond structures would relax the requirements for full PBG, as far as dielectric contrast is concerned reducing it to as low as 4. This fact would open the possibility of using transparent materials to produce 3D full PBG in the visible range. Making use of oppositely charge polymer particles it is possible to realize more complex crystalline structures.^[175] Recently, Hynninen *et al.* have proposed the use of colloids of different nature to realize diamond or pyroclor lattices.^[176] The idea, already proposed by F. García-Santamaría *et al.*,^[177] consists of building body-centred-cubic structures composed by two types of spheres (SiO₂ and PMMA) that can be selectively etched to render the desired diamond structure.

In summary, a number of different techniques have been developed over the last few years to obtain self-assembled structures for photonic applications (See Table 1). Which of them is the most appropriate will depend on the particular use: the Vertical deposition method provides the highest optical quality and therefore it should be chosen when fundamental optical properties are going to be studied or exploited; Spin-coating casting should be considered for large-scale preparation. In any case, one should also check a variety of recent reviews on this topic to make sure which type of preparation procedures better suits one's particular requirements.^[178,179]

3.2. Disordered Structures

While (ordered) periodic photonic media take advantage from the periodicity in the dielectric constant and the consequent

Table 1. Summary of most used self-assembly techniques.

Type	Thickness	Area	Time	Optical Quality	Issues
Sedimentation ^[127]	mm	mm ²	weeks	poor	fragile, material waste
Cell confinement ^[130]	few to tens of monolayers	mm ²	1–2 days	good	opening the cell
Vertical Deposition ^[132]	1 to tens of monolayers	mm ²	1–2 days	excellent	large beads plummet
Langmuir-Blodgett ^[146]	1 to several monolayers	dm ²	hours	poor	sequential
Shear induced ^[158]	mm	dm ²	minutes	poor	polycrystalline, high amount needed
Motor drawing ^[142]	1 to tens of monolayers	mm ²	hours	good	high concentrations needed
Air-water interface ^[153]	few to tens of monolayers	mm ²	minutes	fair	indetermined orientation, substrate detached
Spin-Coating ^[154]	1 to tens of monolayers	wafer size	minutes	fair	polycrystalline
Wedge-Cell ^[145]	1 monolayer	cm ²	hours	excellent	only 2D

long-range correlation, disordered ones, with no positional order, can still strongly affect light transport.^[180] Typical examples of disordered photonic media are white paint, bones or fog. While fully random media are materials that lack any structural correlation or periodicity, the general class of disordered media includes topological arrangements with long or short range correlation, but with no full periodicity. Among the latter, fractal media,^[181] which have self-similar geometries, quasi-periodic,^[182,183] which are arranged in orderly patterns that are not quite crystalline, and controlled disordered PCs,^[184,185] or non-isotropic complex fluids like nematic liquid crystals,^[186] have the potential to combining the qualities of both random and periodic systems.

Despite the fact that recently artificial random media with novel properties like polymer dispersed liquid crystals,^[187] chemically etched porous GaP^[188] and Silicon, or Levy glasses,^[189] have been proposed, still a broad materials science effort into disordered photonics is lacking. Although an amount of interesting physical phenomena arise from the study of those systems, such as coherent light back-scattering,^[190,191] random lasing,^[192] strong light localization^[193] in relation with electrons localization^[194] or long range intensity correlations,^[195] these experiments have been mainly focussed on materials like “white paints”: oxides or semiconductor powders for the visible such as TiO₂^[196] and ZnO,^[197] or for the infrared as GaAs^[198] or Germanium.^[199] They all are formed by particles with casual shapes and sizes, always with a mean size of the order of the light wavelength. Materials composed by polydisperse spherical particles have also been available, presented both in solid arrangements such as Al₂O₃,^[200] ZnO,^[201] or TiO₂^[202,203] as well as in colloidal suspensions.^[204,205] In all these cases, the particles composing the system are polydisperse in shape, size or both and the individual electromagnetic response of each building block give rise to an averaged-out optical response.

The class of quasicrystals^[206] belongs to the intermediate regime between periodic and random arrangements. In these deterministic non-periodic structures, translational symmetry is absent, while long range correlation can still exist. For these properties quasicrystals are also defined as deterministic complex media without translational invariance.

Another important class of disordered media grown by self-assembly is the class of aerogels.^[207] Aerogels are obtained by liquid extraction at the critical temperature for which two phases are present at any time.^[208] Due to the very low filling fraction of these materials, which can easily be less than 1%, the scattering strength is weak, making aerogels suitable for single-scattering studies rather than multiple-scattering and light diffusion. Standard aerogels have particles of 1–10 nm, and recently even

aerogels of large particles, ~100 μm have been obtained by means of microgravity in parabolic flights.^[209]

Effective design of novel disordered material can either focus on the topological structure of the scattering particles, i.e. on the type of disorder and its optical correlations, or on the optical properties of the microscopic building block. The recently proposed Levy glasses^[189] are an example of a topological structured medium with non-random distribution of scatterers, while photonic glasses,^[210] a solid random arrangement of monodisperse (within 2%) spheres, extend the control over light diffusion via the optical resonances of the building block.^[211]

Photonic glasses share the same microscopic constituent as PCs, the dielectric sphere, but with a crucial topological difference, disorder instead of order. **Figure 4a** shows how the topological difference between a photonic glass and a PC leads to very different interference optical properties. A simple light transmission experiment can give a diffraction pattern for a PC (Figure 4b) or a speckle pattern, a granular distribution

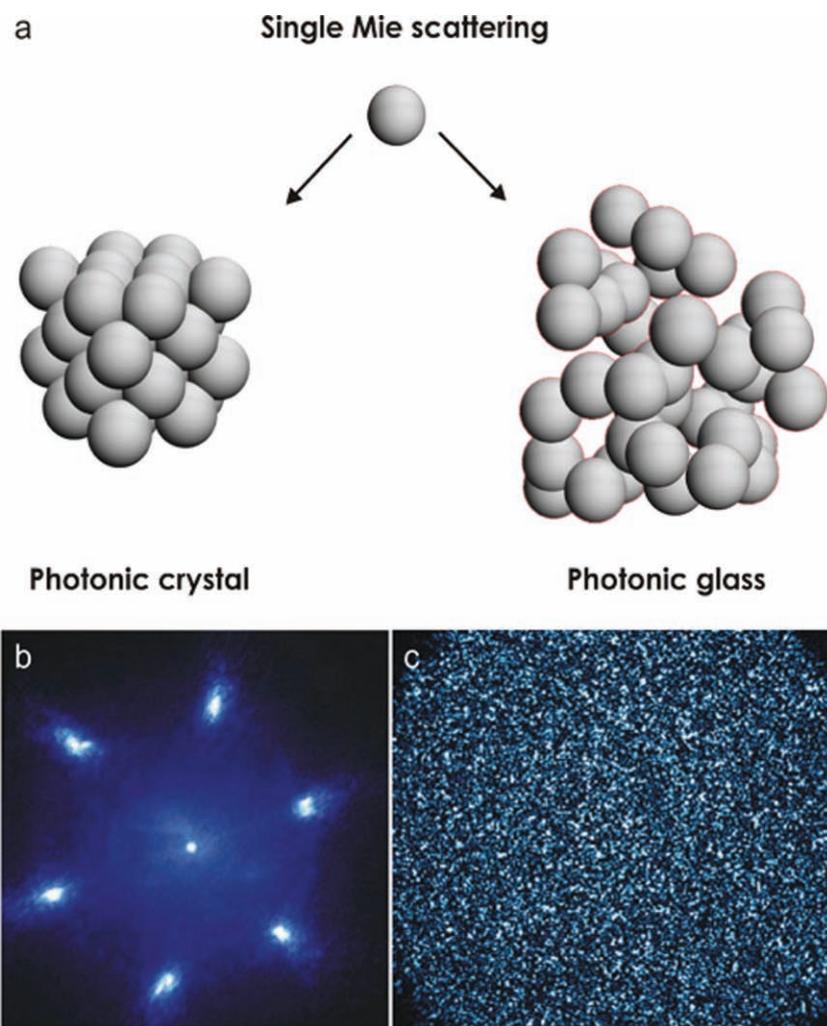


Figure 4. (a) Ordered and disordered packing of a single-scattering particle, a dielectric sphere in this case. (b) and (c) light speckle pattern arising from an ordered fcc arrangement of dielectric microspheres and from a random arrangement of the same spheres, respectively, illuminated with a laser and imaged on a far field screen. Used with permission from [5].

of light intensity, for a photonic glass (Figure 4c). Photonic glasses have been demonstrated to be a perfect playground to observe dispersive light diffusion in the same system, a crucial combination that allows controlling light diffusion as PCs do for ballistic light. From the interplay between diffuse light and designed-disordered several effects may be affected as, for example, the possibility of self-tuned random lasers^[212] or resonance-dependent Anderson localization.

In order to completely achieve random disorder one has to force the flocculation of the spheres and to induce the formation of random clusters, preventing the spheres from ordering. Spheres remain isolated in a stable colloid owing to their surface charge, which ensures the suspension stability through electrostatic repulsion, preventing them from sticking.^[213,214] If two particles collide, they will stick together and make a larger particle or, eventually, a cluster. Clusters get larger than the critical size to be suspended and settle. Adding extra charge (electrolytes) balances the surface charge and renders the particles neutral allowing them to form clusters that plummet to the bottom and aggregate as a glass. The size of the clusters has an important effect on the filling fraction, f , of the system and may strongly affect the physical magnitudes which describe light transport. It has been shown that, increasing the electrolyte concentration, glasses where clusters present increasing sizes can be grown.

4. Further Processing

Templating^[215] is a usual technique in materials science that permits the structuration of materials at different scales, from nanometres to micrometres. Using hosts of different nature to include other compounds (guests), replicas are created after the sacrificial scaffold is safely removed or subsequent growth is facilitated the desired manner.^[216] This technique has revealed very functional to replicate biological specimens with particular useful features that are otherwise hard to obtain by synthetic means. These biological scaffolds are being used to produce many different nanomaterials for a number of distinct applications since the last few years.^[217] Biotemplating opens the possibility to create novel photonic structures like those mimicking structural properties of butterfly wings^[218] in Al_2O_3 ^[219] or GeSbSe chalcogenide glass.^[220] Very recently, photonic scales of the weevil *L. augustus* have been converted into high-dielectric TiO_2 replica, having diamond structure.^[221]

Bare opals, either SiO_2 or polymer, are frequently used as templates. This is due to the fact that their low refractive index contrast provides weak photonic effects and, that they cannot open a full PBG. When PCs field emerged 20 years ago, the experimental *holy grail* was to obtain structures with complete gaps. Later on, some other interesting phenomena not associated to the existence of a full PBG have appeared, spreading the uses of such systems not only to increase their photonic strength (dielectric contrast) but also to exploit other functionalities such as slow light,^[222,223] super-refraction^[224,225] or negative dispersion.^[226] When Sozuer *et al.*^[227] demonstrated the existence of a full PBG for fcc structures between the 8th and the 9th photonic bands, provided a dielectric contrast higher than 8.7 (air spheres in a high index background), the challenge was

to modify these materials composing the artificial structure to fulfil those requirements. After some attempts^[228,229] a full PBG in the optical range (precisely at 1.5 micrometres) based on colloidal PCs was finally achieved in silicon inverse opals.^[230] Since then, the ultimate challenge in this kind of structures has been minimizing intrinsic defects and controlling intentionally added defects. On the one hand, unwanted defects are common in self-assembled structures and they are hard to avoid. On the other hand, controlled defects are in fact much harder to achieve due to the way these crystals grow. However, since the last few years some approaches have been taken to deal with both, improving sample quality and introducing controlled defects as will be discussed in the following with some examples. In Figure 5a typical procedure for templating in opals is shown.

4.1. Infiltration

Bare opals are often used as templates (raw material) for further processing, including patterning, to produce cavities or waveguides or simply to shape and expose particular facets, and infiltration, to increase refractive index contrast or to introduce active elements as non linear or luminescent materials, both combining “bottom-up” and “top-down” approaches. Since the very moment artificial opals were proposed as 3D PCs it was obvious that they should be combined with other materials to boost their potential, either by increasing their dielectric contrast or by incorporating active elements, chiefly emitters, to modify spontaneous emission in the search of low-threshold laser sources. This pursuit has favoured the enormous development observed in the last few years regarding experimental realizations of opal-composites of a large variety of materials, pushing and enriching the state of the art in materials science.

Although the first work on self-assembled 3D PCs already dealt with the possibility of modifying the spontaneous emission of CdS quantum dots infilled in opaline structures,^[126] increasing dielectric contrast was the target of most of the initial work on this subject. The essential challenge is to increase dielectric contrast maintaining transparency. This is the reason why early work focused on TiO_2 ^[229,231] and later on research moved to the near infrared with silicon^[232] and germanium.^[233] Very different techniques have been employed to grow materials within the pores of the opaline structures over the last few years. They can be divided into two categories according to whether the material is grown (synthesized) inside the structure (*chemical infiltration*) or it is only infiltrated having been prepared earlier on (*physical infiltration*).

In the first case the inner surface of the template can help not only in shaping the composite but also in controlling the synthesis reaction. In the latter case the template only acts as a scaffolding from where the guest material gets its form.

4.1.1. Physical Infiltration

Obviously materials apt to be physically infiltrated must be in the form of nanoparticles suspensions or molecular solutions since they must be smaller than the pores of the template they are meant to impregnate. The usual way of infiltrating materials already synthesized is by just dipping the porous structure into

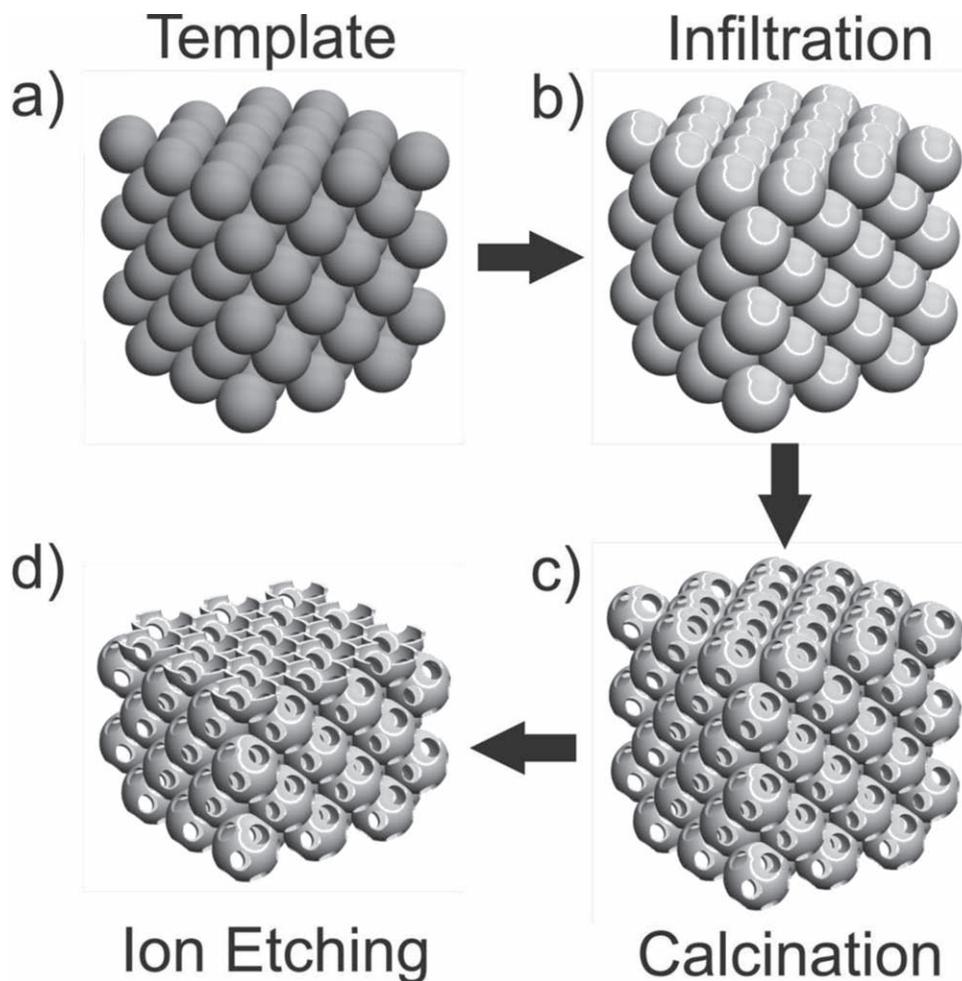


Figure 5. Templating and processing. After assembly of polymer beads (a); the template is infiltrated by ALD or CVD (b); Polymer beads can be etched away by calcination (c); Further anisotropic etching by ion beams can improve sample surface termination (d).

a solution containing the material to be infiltrated. This method has been used to introduce organic dyes just by dropping the solution containing the dyes onto the opal. Sometimes it becomes necessary to force pump the solution through the opal pores to increase the infiltration efficiency like in the case of CdSe quantum dots,^[234] and the process yields rather inhomogeneous structures. One alternative to improve homogeneity is dip-coating, a technique that can be performed directly during the growth by vertical deposition mixing the particles forming the opal and the ones to be infiltrated.^[235] By this method the homogeneity is far superior and it allowed the preparation of ultralow dielectric constant films out of SiO₂ nanoparticles templated on polystyrene opals.^[236] Similar co-deposition procedure was followed to infiltrate CdSe and CdTe quantum dots in opal structures.^[237] Step-motor assisted dip-coating has also been recently used to infiltrate semiconductor quantum dots (CdTe, CdSe, PbS) with better homogeneity.^[238,239] Casting a solution by spin-coating is also an alternative which has yielded homogeneous replicas of mesoporous colloidal crystals^[240] and rare-earth oxide nanoparticles.^[241]

Other different approaches combine nanoparticles (semiconductor, magnetic, metallic, etc) with beads^[242] preparing

building blocks for further crystallization. These methods include deposition of particles around the spheres (core-shell) by means of layer-by-layer (LBL) technique^[69] or preparing mixed colloids by encapsulation^[243] or by using microgels^[244] as functional colloidal materials.

4.1.2. Chemical Infiltration

Chemical infiltration entails transporting the chemicals to the reaction site and the residues outside. Since the reaction must take place in hundreds of nanometres pores forming a network and connected through necks often tens of nanometres it must be realized that the access is awkward to say the least. Furthermore, if the material grows on the walls of the pore it is readily understood that the access port diminishes in size as the reaction proceeds putting a limit to what thicknesses can be grown.

Initial experiments dealt with wet chemistry methods such as chemical bath deposition,^[245] sol-gel^[246] or electrodeposition^[247] obtaining rather granular structures with low optical quality. The latter has been widely used to infiltrate a large variety of metals into colloidal matrices creating both 2D (metallic

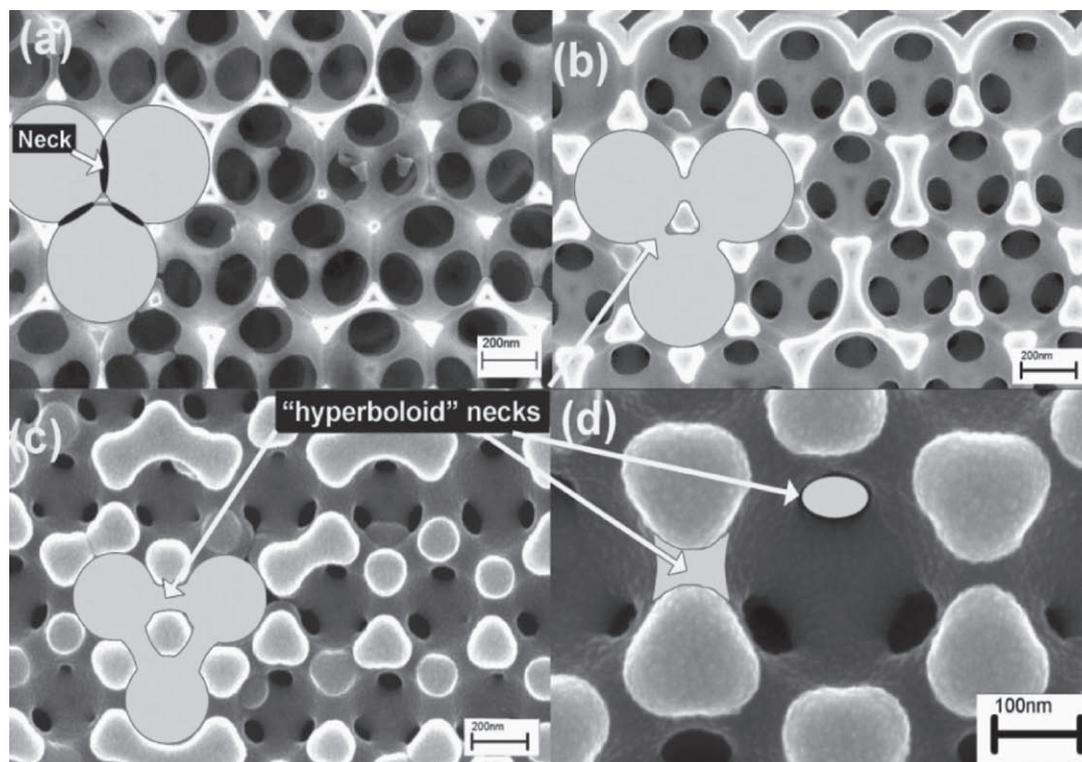


Figure 6. Infiltration of TiO_2 by Atomic layer deposition (from reference [261]). This technique permits fine control (and tuning) of the structure filling fraction due to the extremely high precision of the infiltration. High quality replicas are obtained for a variety of materials, mainly oxides.

gratings) and 3D structures of gold,^[248] silver,^[249] nickel,^[250] zinc,^[251] etc., most of them exploited as metallodielectric crystals and magnetic or plasmonic networks. Interesting II–VI and III–V semiconductors, including GaAs, have also been electrodeposited in this kind of structures.^[252] Recently, high quality germanium inverse opals have been prepared by this technique.^[253]

Lately, gas based methods such as chemical vapour deposition (CVD) or atomic layer deposition (ALD) have revealed much more versatile producing materials of higher quality. CVD is a powerful method to infiltrate colloidal PCs and it has been used to grow a variety of materials, most of them high refractive index semiconductors. Initial experiments dealt with binary compounds such as InP,^[254] TiO_2 ,^[255] or GaP,^[256] but the major achievements have been obtained when dealing with single compounds such as silicon^[230] or germanium.^[233] This process provides very conformal layers around the spheres of controllable thickness, essential to control the filling fraction, and good homogeneity. The only drawback of this technique is the relatively high temperatures needed (above 220 °C in the case of silicon) which limits the usable templates. In particular, for organic colloidal crystals (polystyrene or PMMA) it is first necessary to protect the structure growing an additional inorganic layer (mainly SiO_2) at room temperature to produce resilient templates for further processing.^[257,258] Room temperature CVD has been used to grow SiO_2 in opals to increase their mechanical stability,^[259] and ZnO in polystyrene structures.^[260] Here, the precursor (silicon tetrachloride) in the case of SiO_2 or dimethyl zinc for ZnO) is hydrolyzed in the presence of water, the reaction being very similar to that occurring

in commercial ALD systems. By this latter method very homogeneous inverse opals can be obtained of TiO_2 ^[261] and ZnO^[262] with an extremely precise control in shell thickness (around 1 angstrom per cycle) and at rather low temperatures, compatible with organic templates (Figure 6).

All the methods mentioned above modify the original structure by growing a variety of materials within the opal matrix. Very recently, a completely new way of modifying the composition of these photonic templates has been developed. It basically consists on reducing SiO_2 direct opals to silicon by the help of magnesiothermic reduction combined with CVD. This new procedure produces high quality silicon direct opals.^[263]

4.2. Defects

Initial attempts to introduce controlled defects in self-assembly colloidal crystals were performed by doping ordered colloidal suspensions with particles of a different size.^[264] By introducing larger (smaller) spheres into the suspensions donor (acceptor) defect states were created inside the photonic gap. Since then, a large variety of strategies have been developed to realize controlled defects to engineer light propagation in this kind of structures, a must if one aims to exploit all the possibilities these systems can offer in terms of functionality.^[184,185]

Planar defects (2D) are probably the easiest way of perturbing the periodic arrangement in artificial opals due to the way they naturally grow (Figure 7b). The vertical deposition method allows the modification of the lattice parameter by growing

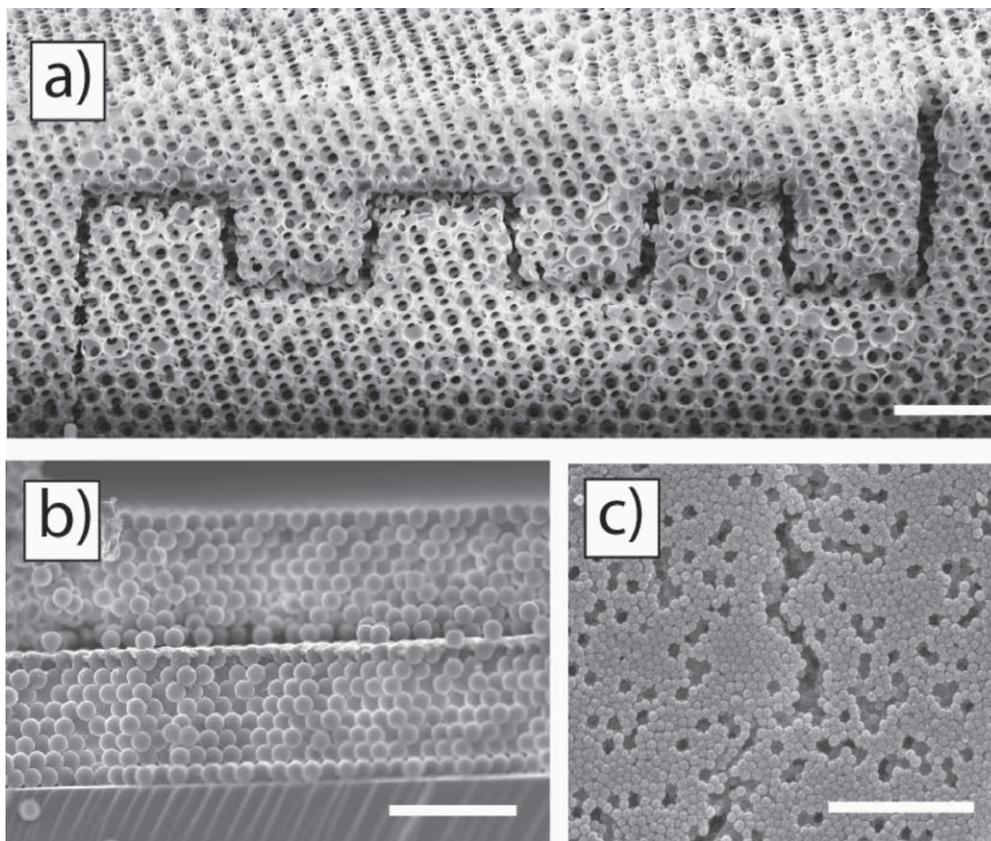


Figure 7. SEM images of engineered defects in self-assembled photonic materials. (a) Line defect introduced in a silicon inverse opal by means of a multi-step process involving two-photon polymerization, (b) artificial opal containing a planar defect grown by spin coating a nanoparticle suspension (c) lattice of point defects introduced in a PMMA thin film opal by selectively removing PS spheres. Images (a), (b) and (c) have been reproduced with permission from [210,271,284], respectively. Scale bars correspond to 2, 5, and 4 μm for figures (a), (b) and (c) respectively.

layers with different sphere sizes producing superlattices^[265,266] and other opaline heterostructures.^[267] The possibilities grow when introducing different materials: Interfacial SiO_2 layers of controlled thickness grown by CVD can be buried between two inverse opal structures opening defects modes in the opal pseudogaps,^[268,269] which can be further tuned if active materials are used instead of SiO_2 .^[270] This kind of defects are also possible by “spin-coating”, which adds functionality due to the variety of new materials (i.e. nanocrystals) that can be incorporated as a “defect” within the opal structure.^[271]

Lithographic techniques have been used to pattern substrates (to direct colloidal crystallization) or to control and engineer point, line and planar defects.^[272] In order to have a total control on light propagation it is very important to be able to direct the growth of artificial opals on designed patterns and some approaches have been taken to fabricate photonic chips^[273,274] combining micro-fluidic techniques and soft lithography.^[275,276] It is possible to define patterns on stamps to produce colloidal motives by nanoimprint.^[277] PMMA opals can be patterned through e-beam lithography,^[278–280] a technique which is compatible with standard microelectronics procedures and therefore interesting for further devices fabrication.

Point defects (missing spheres or specific modification of some of them) are inherent in artificial opals and they can randomly

made to occur. Introducing larger (smaller) spheres as dopants it is possible to study disorder in these structures.^[281] Further, by combining PS and PMMA spheres and selectively etching one of them it is possible to prepare structures with the desired amount of vacancies, provoking correlated disorder (Figure 7c).^[210]

The next natural step is producing line defects (waveguides). Best approaches into this direction have taken advantage of Direct Laser Writing technique.^[282] By embedding the voids of an artificial opal with photosensitive resins it is possible to draw lines by two photon absorption polymerization of the exposed areas that can be selectively developed,^[283] creating 3D waveguides and cavities within the opal network. Furthermore, these engineered opal structures can be further processed in silicon, constituting the most advanced approach to 3D controlled defects for this kind of structures (Figure 7a).^[284]

5. Propagation and Emission in Self Assembled PCs

The optical properties of a medium are not only determined by the response of its isolated constituents but also by its spatial arrangement. In particular, the influence of the periodic structure on the electromagnetic response of the medium can lead to profound modifications as compared with those of an equivalent homogeneous medium.

The influence of the arrangement of the composing microstructures is so strong that it is the origin of concepts such as photonic crystal and photonic glass. Since the former and its optical properties are nowadays relatively familiar we chose to treat the latter in a separate section.

The optical response of PCs can be understood to a large extent by considering the PC as a true infinite and perfectly periodic structure made of non absorbing dielectric materials. These assumptions lead to the band structure of the material which is summarized in the following paragraphs. For a more detailed derivation of the band structure, its meaning and implications on the photonic properties of PC's, we refer the reader to standard text books^[222,285] or recent review articles.^[9,286]

We consider the electromagnetic wave equation for the magnetic field \mathbf{H}

$$\nabla \times \left[\frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right] = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}). \quad (1)$$

This (plus transversality conditions) is an hermitean eigenvalue problem on the magnetic field if the relative permittivity of the medium $\epsilon(\mathbf{r})$ is purely real (no absorption). If the spatial dependence of $\epsilon(\mathbf{r})$ corresponds to that of a periodic lattice, then solutions to the eigenvalue problem (1) can be cast in the form of Bloch waves $H_{k,n}(\mathbf{r})$ with eigenfrequencies $\omega_n(\mathbf{k})$. Where n refers to the band index, and \mathbf{k} to the Bloch's wave vector: something like the wavevector of plane waves.

The dispersion relation $\omega_n(\mathbf{k})$, known as the crystal's band structure, and the structure of the eigenmodes, determine all the light transport and emission properties of the PC. Several aspects must be highlighted at this point.

Perhaps the chief feature of the band structure is the appearance of gaps as can be seen in the example shown in Figure 9c. Frequency regions in which a limited set of modes is available, or even a total absence. The opening of a band gap forbids the propagation of electromagnetic waves in these frequency ranges while, complementarily, the emission of light is also precluded or fundamentally modified.

The effect then of the band structure is to strongly modify the spectral and angular properties of transport and emission of light in PC's.

When the quality of the crystal is poor, disorder appears and induces several intriguing effects in the light transport and emission properties of such disordered self-assembled structures. We shall consider this subject in Section 6.

5.1. Light Propagation in PC

Real crystals are of course finite structures, and are subjected to imperfections. Nevertheless the dispersion relation of a crystal provides important insights in the understanding of the transport properties of a real PC. Reciprocally, transport measurements offer information about the photonic structure of the studied material.

In the low energy region, the dispersion relation of the crystal is almost linear; hence, it behaves like a homogeneous medium. Experiments performed on slabs of PC will then resemble those performed on slabs of a homogeneous

medium and can serve to obtain information about the actual filling fraction of the crystal, structural properties and topology of the lattice. Among those, most important in this respect, is the possibility to describe the medium through an effective refractive index which acquires an imaginary part only where extinction appears, in this case through Bragg reflection.^[287]

Higher in the frequency domain, a stop band typically opens in a certain region of the reciprocal space. In fcc structures the first gap opens in the Γ -L direction, hence transmission at frequencies lying in this region is strongly inhibited, giving rise to a dip in transmittance and a peak in reflectance (see Figure 8). The study of these features in transmission and reflection give information about the position of the band edges and hence, reflection and transmission spectra have become customary techniques for probing the optical properties of self assembled photonic materials. Early work on colloidal crystals,^[288] artificial opals^[126] and inverse opals^[289] employed reflection and transmission spectra to map the dispersion of the L-pseudogap in the surroundings of the L point in reciprocal space. Analogously, reflectance spectra were used to determine the presence of higher order stop bands^[290] and also the full PBG^[230,232,291] in inverse opals. More complicated features of the band structure have also been reported and can be interpreted as anticrossings of the L-pseudogap with stop bands arising from one^[292,293] or more families of planes simultaneously.^[294]

An alternative way to map the dispersion of stop bands is by measuring the emission of broadband internal emitters, i.e. emitting species whose emission spectrum is broader than the spectral width of the stop band. In this case, stop bands appear as dips in the emission spectrum evidencing the redistribution of light emission as a consequence of Bragg diffraction. The dispersion of stop bands has also been observed from emission spectra in several types of self assembled structures such as colloidal crystals,^[295] opals,^[296] composites^[245] or inverse opals.^[297] In the latter, evidence of anticrossings between stop bands due to multiple Bragg diffraction was also observed.

When the frequencies, and hence incoming wave vectors, are sufficiently large, the diffraction onset is achieved. Scattering from an incoming wavevector \mathbf{k} to an outgoing one \mathbf{k}' such that $\mathbf{k}-\mathbf{k}' = \mathbf{G}$, \mathbf{G} being a reciprocal lattice vector, are allowed. In this situation light is neither ballistically transmitted nor specularly reflected, but undergoes Bragg diffraction by other families of planes. In this scenario, the presence of a dip (or a peak) in the above mentioned experiments does not necessarily imply the existence of a forbidden interval.^[298,299] Hence one has to check other directions of light propagation than the forward ones.^[305]

When dealing with transmission of light through finite PC one has to consider not only its band structure but also the coupling of the electromagnetic modes of the crystal to the incoming light. If the incoming light has a spatial distribution which is orthogonal, or weakly overlapping, with the crystal's modal structure, the coupling is inefficient, and hence, low transmittance would be obtained.^[301,302] Another scenario where features in reflection and transmission spectra cannot be associated with the bulk dispersion relation has been presented recently in the form of surface effects present in composite and inverse opals^[303] which could hamper the observation of stop bands and eventually a full PBG.^[304] Finally, reflection

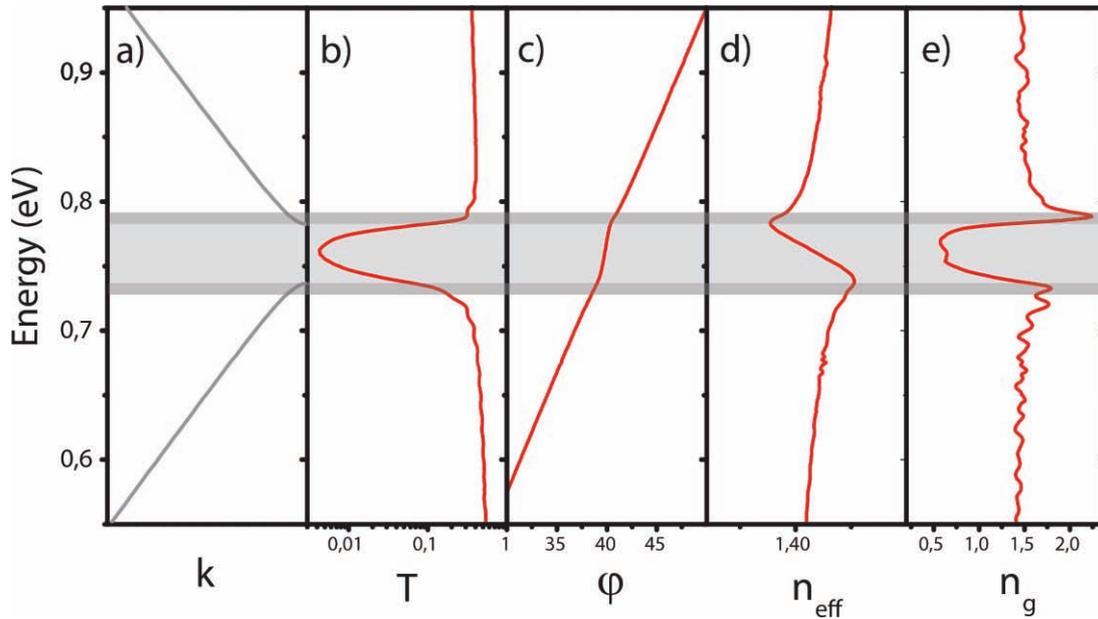


Figure 8. Optical response of an artificial opal measured by conventional and phase sensitive spectroscopy along the ΓL direction in reciprocal space. (a) Calculated energy bands, (b) linear transmission, (c) absolute phase, (d) effective refractive index and (e) group index. Light grey box indicates the spectral width of the pseudogap. Dark grey bands indicate the pseudogap edges. Adapted from [287].

and transmission spectra have also been employed to investigate the presence of localized defect states within the pseudogap associated with intentionally placed point and planar cavities.^[264,268,269]

The interest in mapping the dispersion relation of a PC lies on the fact that it imposes strong modifications on the radiation-matter interaction. The modal structure of electromagnetic fields in PCs can provide information about this interaction. Hence, mapping the dispersion relation of a PC is an important subject in the determination of the optical properties of a sample.

If one wishes to probe the dispersion of allowed energy bands rather than the presence of stop bands, the use of reflection or transmission spectra is quite limited. Although for such spectral intervals the sample is transparent, non uniform sample surfaces and diffuse scattering by defects hampers the observation of Fabry-Perot fringes from which the band dispersion can be inferred. It is only for thin samples or samples having a small refractive index contrast that reflection and transmission measurements can provide information on allowed band dispersion, as shown in reference^[306] for opals in the surroundings of the L-pseudogap. In order to explore the dispersion of photonic bands several alternative techniques have emerged over the past decade.

The energy velocity, equal to the group velocity in an infinite PC,^[222] can be dramatically altered in a PC. At the band edges, the dispersion relation along certain directions is nearly flat. Hence in these regions, the group velocity for the considered band n , $v_g(k, n) = \nabla_k \omega_n(k)$, can be extremely small, leading to an enhanced radiation-matter interaction. The inverse of the group velocity modulus is proportional to the number of available modes at a given frequency and value of \mathbf{k} , or density of states, as described in the next subsection. Hence, increasing the number of states involves increasing the radiation matter interaction. In an intuitive fashion, it can be argued that the

slower the radiation speed (group velocity) the larger the interaction time (Radiation-matter interaction).

This fact leads to several consequences. Scattering by imperfections at those frequencies can be much stronger than in vacuum, hence the scattering mean free path^[307] or the diffusion constant^[308] can be severely reduced. As first noted in the pioneering work by S. John^[4] this fact could lead to strong localization of light in 3D weakly disordered PC's.

The regions of low v_g at the edges of a pseudogap were probed by measuring the slowing down of ultrashort pulses using time of flight^[309] and phase sensitive techniques^[310] in 3D PC of reduced refractive index contrast. The same spectral region was also studied with a Michelson interferometer and monochromatic light to retrieve the phase delay of light transmitted from colloidal crystals both, perfectly ordered^[311] and containing point defects.^[312] White light interferometry has been extensively used recently to retrieve the optical phase in transmission experiments on artificial opals. From the measured phase information, both v_g and effective refractive index have been obtained in a wide spectral region around the pseudogap (see Figure 8). Samples with different topologies have been studied including ordered artificial opals oriented along different crystallographic directions^[287,313,314] and opals containing planar defects.^[315] Recently, measurements in the high energy region of artificial opals have revealed the existence of slow and superluminal values of v_g , though in this region obtaining a univocal relationship between measured phase and energy bands is not an easy task.^[316]

The enhanced radiation-matter interaction leads to strong modifications of the emission dynamics in PC. Also, the possibility of tailoring the radiation-matter interaction opens the way to applications ranging from photochemistry to lasing as we shall consider in the next sections.

5.2. Light Emission in PC

Since the pioneering work of Yablonovitch^[3] it has been recognized that spontaneous emission can be dramatically affected by the modal structure of the PC, the most extreme case being its complete inhibition.

An isolated quantum system (atom, molecule, quantum dot) possesses a certain spectrum of energy levels. Once the system is prepared in a pure eigenstate, its temporal evolution is rather trivial: it persists unperturbed in the same state as the eigenstates are perfectly stable. This picture breaks down when the interaction of the atomic system with other entities is considered. In particular, the unavoidable interaction of the system with the electromagnetic field vacuum fluctuations has several effects in the quantum system. Its spectrum is modified (Lamb shift) and the eigenstates of the isolated atomic system are no longer stable, but rather meta-stable, having a definite lifetime. It is of paramount importance to elucidate the dynamical properties of a quantum system – an emitter- coupled to the, eventually modified, electromagnetic vacuum.

5.2.1. Spontaneous Emission in PC

Spontaneous emission is a process through which an emitter excited from its ground state to an excited one relaxes through its coupling with external degrees of freedom introduced by the electromagnetic field, among others, and a photon is created. Generally, both ground and excited states are split in numerous sublevels, and the dynamics governing transitions among sublevels can be considered fast enough to neglect its associated lifetimes. As a result, the absorption and emission spectra of a fluorescent emitter are shifted. This is known as Stokes shift. Essentially, the spectral and dynamical properties of photoluminescence depend on the optical response of the medium surrounding the emitter. Although the role of environment on relaxation dynamics is well known since a long time ago,^[317] the effects of a PC are much more modern a subject,^[3] and only recently the full picture of photoluminescence in PC has become clear.

The simplest model accounting for spontaneous emission considers the emitter as a two level system with a given transition (emission) frequency ω and an expected value of its electric dipole moment $p = \langle \Psi_e | e r | \Psi_g \rangle$. Where Ψ_e, g denotes the emitter's excited and ground states respectively and e is the electron's charge magnitude. If the emitter is coupled to the electromagnetic field through only (electric) dipolar interaction, the atom prepared in the excited state at time $t = 0$ undergoes a relaxation process through the emission of a photon of frequency ω . Considering that the coupling strength is weak enough (weak coupling regime), the probability of emitting a photon as a function of time decays exponentially with time, being Γ the decay rate.

The decay rate can be accounted for through classical considerations, as Γ is proportional to the total power radiated by a classical point dipole p with resonant frequency ω . In particular the classical optical response of the PC described by its Green's tensor, provides information about the lifetime^[318,319] and Lamb shift^[320] of emitters immersed in PC's.

In the following subsections we introduce different definitions of density of electromagnetic states in connection with the radiation emission by a classical emitter, and its relation with fluorescence phenomena in PC's.

5.2.2. Classical Dipole Radiation in a PC. The Role of Density of States

The simplest model of a classical point dipole emitter, a classical oscillating electric dipole,^[321] in a PC is far from being a toy model but provides valuable information about emission dynamics in real systems.^[322] Considering a point dipole p oscillating at frequency ω , the determination of its dynamical properties (eg. emitted power) and the angular emission spectrum can be performed by using the electric Green tensor of the system in the frequency domain $G^E(r, r', \omega)$. A PC being a non-homogeneous and non-isotropic system, the emission properties of such a system will depend on both the position and orientation of the emitter with respect to the lattice.

The field created at the point r by such a classical point source placed at r' is $E(r) = \omega^2 \mu_0 G^E(r, r', \omega) p$.^[321] This equation describes the coupling of the source to the available electromagnetic modes in the system to radiate in the direction given by r .

If the dipole $p = p \hat{u}$ points in the direction \hat{u} , then the radiated power is $P_R = \frac{p^2 \omega^3 \mu_0 \text{Im}[\hat{u}^\dagger G^E(r, r', \omega) \hat{u}]}{2}$.^[323] The Green tensor of the system possesses hence all the information about the emission properties of a point dipole. In a PC it can be written as a superposition of eigenmodes,^[222] formally as $G^E(r, r', \omega) = \sum_n \int_{1BZ} d^3k G_{k,n}^E(r, r', \omega)$, where the integral comprises all Bloch k vectors in the first Brillouin zone and the sum all bands n at the frequency ω . Each contribution to the sum is a tensor product of eigenmodes of the system with the appropriate weight.

The power radiated by the point dipole depends on its position, orientation, frequency, and possess an angular distribution determined by the modal structure and the number of available electromagnetic fields at the position of the emitter, the so called density of electromagnetic states (see **Figure 9**). Although a unified terminology in the literature does not exist, we shall introduce some definitions of different density of states functions in the following paragraphs establishing a link between optical response of the medium and the emission properties of a point dipole emitter.

The projected local radiative density of states (PLRDOS), denoted here as $D_{\text{rad}}(r, \omega, \hat{u})$, accounts for the number of electromagnetic states available for the emitter to couple to per unit volume and unit frequency at the position of the emitter. Projected, in this context, refers to the emitter orientation \hat{u} . It can be related to the Green tensor by

$$D_{\text{rad}}(r, \omega, \hat{u}) = \frac{3\omega}{\pi c^2} \hat{u}^\dagger \text{Im}[G^E(r, r, \omega)] \hat{u}$$

It is worth noting that this is not only a mere count of eigenstates, as it is weighted by the dielectric function at the emitter position.^[324] The emitted power by the point dipole is proportional to the PLRDOS.

Considering the superposition of Bloch modes describing the Green tensor, we define the projected mutual density of

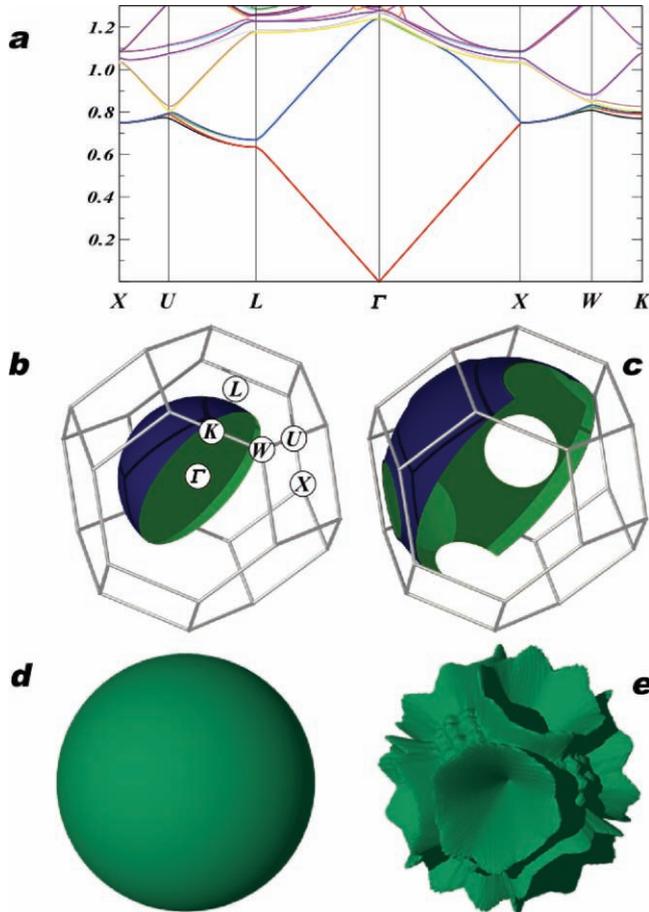


Figure 9. a) Dispersion relations along a path in the reciprocal space passing through several high symmetry points for an fcc lattice made of Polystyrene spheres. b) Sketch of the Brillouin zone (wires) and a cut of the isofrequency $a/\lambda = 0.42$. c) Analogous to b) with $a/\lambda = 0.62$ a gap around the Γ -L direction can be seen. d) and e) are the orientation averaged radiation patterns corresponding to b) and c) respectively for an ensemble of emitters distributed homogeneously in the PC. In e), radiation emission along the (1,1,1) direction is completely inhibited.

states (PMDOS). This quantity describes the radiation angular spectrum of the emitter placed at a point \mathbf{r} at the working frequency.

In analogy with the mutual density of states defined in,^[325] PMDOS is defined as $M(\mathbf{r}, \mathbf{k}, \omega, \hat{\mathbf{u}}) = \frac{3\omega}{\pi c^2} \hat{\mathbf{u}}^i \text{Im}[G_k^E(\mathbf{r}, \mathbf{r}, \omega)] \hat{\mathbf{u}}^i$ (here we drop the band index for simplicity). In the context of fluorescent intensity in PC's, a slight modification of the PMDOS has been termed fractional DOS.^[326]

The (projected) spectral density of states^[325] (PSDOS), defined as the average over the Wigner-Seize cell $S(\mathbf{k}, \omega, \hat{\mathbf{u}}) = V_{\text{WS}}^{-1} \int_{\text{WS}} d^3\mathbf{r} \epsilon(\mathbf{r}) M(\mathbf{r}, \mathbf{k}, \omega, \hat{\mathbf{u}})$, is a measure of the contribution of the different Bloch modes to the total projected density of states (PDOS) $N(\omega, \hat{\mathbf{u}}) = \int d^3\mathbf{k} S(\mathbf{k}, \omega, \hat{\mathbf{u}})$.

It is worth noticing that slight modifications of PSDOS are also termed, in an analogous context, reduced DOS^[327] or, in solid state physics, spectral function.^[328]

In terms of the PLRDOS the PDOS can be expressed as $N(\omega, \hat{\mathbf{u}}) = V_{\text{WS}}^{-1} \int_{\text{WS}} d^3\mathbf{r} \epsilon(\mathbf{r}) D_{\text{rad}}(\mathbf{r}, \omega, \hat{\mathbf{u}})$. We can hence

define a projected local density of states (PLDOS) as $D(\mathbf{r}, \omega, \hat{\mathbf{u}}) = \epsilon(\mathbf{r}) D_{\text{rad}}(\mathbf{r}, \omega, \hat{\mathbf{u}})$. The PLDOS accounts for the total number of electromagnetic states per unit volume and frequency at position \mathbf{r} .

In most experiments of photoluminescence, one has little or no control on orientation and position of emitters. In this case it can be convenient to perform the orientation average on the different projected density of states. In this way, we define (dropping the term "projected") the density of states (DOS) as the orientation average of the PDOS and analogous densities of states.

In the above discussion we have considered a point dipole emitter, hence the electric Green tensor describes the emission process. Nevertheless, the magnetic contribution to the total density of electromagnetic modes has to be taken into account in several cases, in particular when dealing with metals. This contribution to the local density of states may be considerably larger than the electric one.^[329]

As stated above, the fluorescence decay rate Γ is proportional to the emitted power by an equivalent classical source. More precisely, Γ is proportional to the PLRDOS^[324] as both magnitudes can be related through Fermi's golden rule.^[330] The spectral and angular intensity patterns of the fluorescent emission are also governed by the coupling of the (quantum) emitter to the available electromagnetic modes, and hence described by the different DOS.

5.2.3. Spontaneous Emission and Density of States

Controlling the DOS, is one of the main goals of self assembled materials for photonic applications. By tailoring the DOS one can effectively control the emission of active media placed inside the sample. In fact Yablonovitch already mentioned in his pioneering work of 1987^[3] the possibility of using self assembled periodic materials to inhibit the spontaneous emission of atoms or molecules by reducing down to zero the DOS inside the material. This scenario would open the path for fabricating novel devices such as zero (or extremely low) threshold lasers or single photon sources, relevant for quantum information devices. Later it was pointed out by Sprik *et al.*^[324] that one does not necessarily need to reduce the total DOS in the crystal. By reducing to zero the position dependent local radiative density of states (LRDOS) at the exact location where the emitter lays one could also inhibit spontaneous emission. Unfortunately, up to now, such precision in the location of light emitters has not been achieved in self assembled structures due to the nature of the growth process. Light emitters tend to be randomly distributed within the available sample volume and have a random dipole orientation, leading to a complex highly non-exponential decay rate.^[331]

As stated in the previous paragraphs, one way to probe the LDOS of 3D self assembled PCs is to study the radiative decay rate of an internal emitter. Initial efforts to modify the DOS were made employing weakly photonic colloidal crystals,^[332] but the presence of electronic and chemical interactions of the emitting molecules with the surrounding medium hampered a clear observation of the effect of the DOS on the decay rate.^[333] Petrov *et al.*^[334] studied emission from organic dyes in a composite opal of SiO_2 and polymer and claimed a modification

of decay rates, both enhanced and inhibited, originating in a redistribution of the DOS. But the small refractive index contrast present in their system was later argued to be insufficient^[335–337] for such a modification, leading to controversy.^[338] Later, Lodahl *et al.*^[339] presented evidence of the effect of the LDOS in enhancing and inhibiting radiative decay rates of CdSe quantum dots employing a strongly photonic TiO₂ inverse opal with a much larger refractive index contrast than in previous attempts. Alternatively, Koenderink *et al.*^[340] have pointed out that one can obtain information on the LDOS of a 3D self assembled photonic structure by studying the modified continuous wave emission of low quantum efficiency emitters placed inside.

Recently, Barth *et al.*^[326] have explained the strong angular and spectral redistribution of emission from organic dyes observed in artificial opals (see below) in terms of a fractional LDOS rather than the LDOS, corresponding to a weighted spatial average of the above defined MDOS. In this case, only field modes propagating along a certain set of directions are considered, namely those collected in the experimental configuration.

As mentioned above, emission spectra and decay rates have been broadly used to retrieve information on the dispersion of stop bands and the LDOS of 3D ordered self assembled structures. But emission phenomena in self assembled materials are rich as a consequence of the peculiar way in which light propagates through them.

Spontaneous emission spectra in the surroundings of the L-pseudogap present not only dips associated with the existence of a forbidden frequency interval (see Section 5.1), but these are usually accompanied by spectral regions where emission is enhanced.^[341–343] Such complex behaviour has been attributed in the case of thin film opals to the strong spectral and angular redistribution of the MDOS due to the periodic modulation of the refractive index and can be accounted for by the MDOS of the crystal, the so-called fractional LDOS in,^[326] as mentioned above. In the case of bulk opals the effect of diffuse propagation due to disorder seems to be responsible for a similar behaviour (see next section).^[343] Recently, results in the high energy region of multiple diffraction have appeared evidencing similar redistributions with spectral regions of both enhancement and inhibition.^[238,343–345] In this case experimental results were also accounted for by a DOS calculated along a given direction of propagation.^[344]

It is worth mentioning that, although the fluorescence lifetime only depends on the PLRDOS, lifetime measurements are usually performed on assemblies of emitters. Hence, the measured lifetimes are weighted averages^[337] of PLRDOS, if the emitter concentration is suitably chosen, then the PDOS or its orientation averaged DOS can be measured.^[346] Nevertheless, in this way, spurious effects can be obtained. For instance, a dependence of emission lifetimes^[347] can be measured as a function of the observation angles with respect to the crystal. If the PMDOS or MDOS present a strong dependence on both the position and the observation direction (given by the set of relevant Bloch wavevectors \mathbf{k}), the measured signal is built up of different spatial contributions coming from emitters placed at different positions in the crystal and depending on the observation angle. Much more detailed experiments, probably comprising single molecule systems, are desirable to fully

explore the effects of angular, spatial and spectral redistribution of photoluminescence in PC's.

Calculations of the angular radiation pattern in the far field for classical^[348] and quantum^[349] emitters have been carried out. It has been shown that the radiation pattern can present a strong angular dependence whose origin lies in the geometrical characteristics of the dispersion relation. The group velocity vector and the Gaussian curvature of iso-frequency surfaces are relevant in the radiation pattern. In Figure 9d and 9e, averaged emission patterns are shown for two different frequencies.

Models accounting for a more detailed structure of the emitter have been carried out recently including three and four level emitters,^[350–351–352] as well as the strong interaction of electronic and photonic states leading to strong polaronic effects in PC's.^[353] Coherent control of spontaneous emission in PC's has also been theoretically addressed.^[354]

5.2.4. Lasing in PC

Ordered self assembled materials have also been considered as candidates to fabricate a “laser without cavity”, in which spectral regions of low v_g provide enhanced light matter interaction throughout the entire sample. In this direction, Vlasov *et al.* studied emission from artificial opals loaded with QDs and observed a directional modification of the gain spectrum of the QDs which they associated with the presence of the photonic band structure.^[355] Later, enhanced optical gain was measured at the L-pseudogap edges of an opal-TiO₂ composite containing QDs by Maskaly *et al.*^[356] Also for this spectral range, where diffraction by just one set of planes takes place, evidence of lasing action has been reported^[357–359] though in some cases mediated through unwanted defects inside the sample, which precluded establishing a correspondence with low v_g regions taking place at the pseudogap edges. In such cases, determining precisely the lasing wavelength when fabricating the structure may not be immediate. Recently, evidence of band edge lasing in artificial opal based PCs has been presented and the lasing emission tuned with the lattice parameter.^[360] Another approach to observe lasing without a cavity in self assembled PC was introduced by Scharer *et al.* who obtained lasing at low v_g energy bands in the high energy region dominated by multiple Bragg diffraction (see Figure 10). In their case a clear correspondence was established with the band structure of the system and lasing in the UV was measured for ZnO inverse opals.^[361]

Finally, after initial demonstration of modified PL by a PC containing optically active planar defects,^[362] optical cavities for lasing have been recently reported in artificial opals containing tailored planar defects. In these systems two opals^[363] (or an opal and a Bragg stack^[364]) are used as the mirrors to provide the necessary feedback while an optically active 2D defect acts as the cavity providing the gain.

6. Optical Properties of Disordered Systems

For a given assembly of particles with well defined optical response, the collective photonic properties of the system are determined by the topology of its spatial arrangement. In the case of a PC, the periodic structure defines a set of modes in the

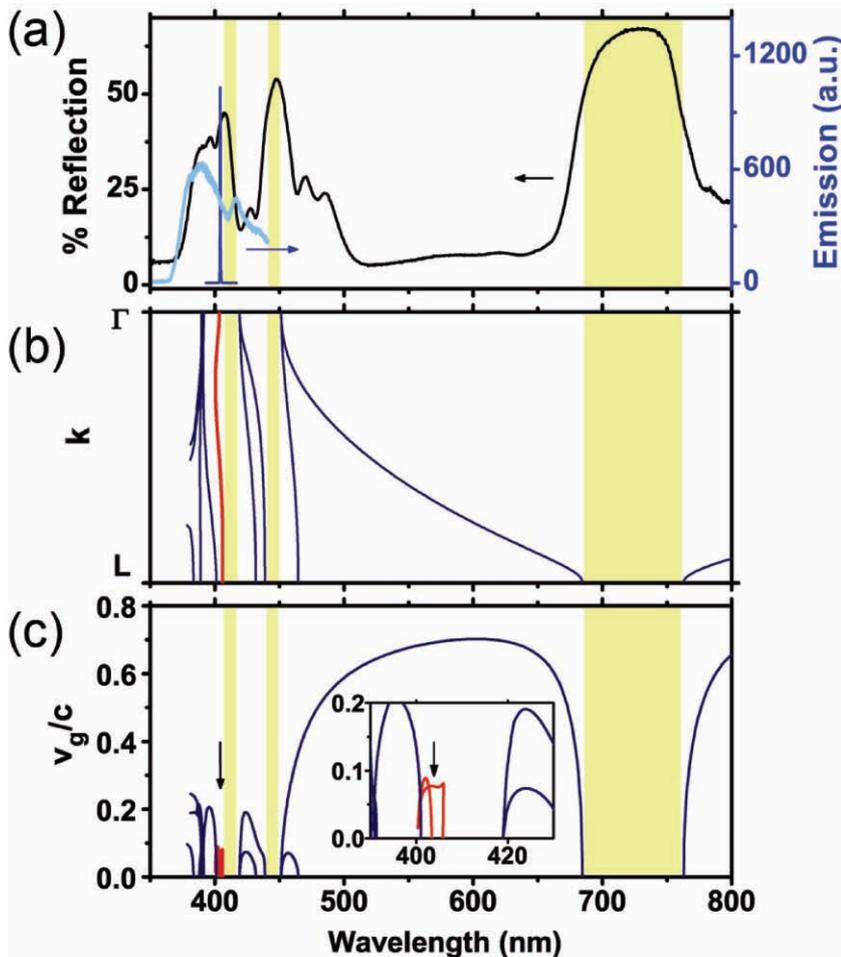


Figure 10. Lasing in a ZnO inverse opal. (a) Reflection (black), photoluminescence (cyan) and lasing spectra (dark blue). (b) Energy bands calculated for the measured sample along the Γ L direction. Low dispersion band associated with laser emission is highlighted in red. (c) Calculated v_g in the spectral range of the energy bands. Inset shows a low v_g region (in red) associated with the flat band shown in figure b). Reproduced with permission.^[361]

lattice and a dispersion relation arises as shown in the previous section. Light transport is described by the band structure in a predictable manner. The opposite of a perfectly ordered structure is of course a completely disordered one. Light transport and emission properties in the latter are dramatically different from those in an ordered structure.

Equations governing light transport and emission in a disordered system are, at the microscopic level, the same, namely Maxwell's equations. Nevertheless, when dealing with disordered systems, a statistical approach is generally more fruitful than a microscopically detailed one. Much resembling the usual approach of statistical physics, the detailed information about the state of a system depends on the precise state of all the degrees of freedom of the system, usually a "macroscopically" large number. Then, retrieving useful information about the system is possible only if a limited set of relevant macroscopic magnitudes is considered. In most cases the average value of the investigated magnitudes is more meaningful than the microscopic details, being at the same time, more accessible. One of simplest and most powerful ways to calculate the

average light transport in disordered media is the diffusion equation.

6.1. Light Diffusion

When light propagates in air or a glass slab, from the source to the detector it does it in a straight line. Light propagation through a homogenous medium is ballistic, that is, propagation direction is not changed during the process. If scattering particles are added to a homogenous film, light propagation direction is more and more randomized. When light travels through a very disordered system, such as that, all of its intensity is multiply scattered, ballistic propagation cannot any more accurately describe the transport of light.

Light passing through a disordered medium, resembles very much the multiple scattering of classical particles placed in a fluctuating random medium like small particles immersed in a liquid. This analogy could be carried one step further considering that light intensity behaves, on average, like the density of an ensemble of small particles placed in a liquid, *i.e.* light intensity will obey a diffusion equation in a random medium:

$$\frac{\partial I(r, t)}{\partial t} = D \nabla^2 I(r, t) - \frac{v}{\ell_a} I(r, t) + S(r, t) \quad (2)$$

This equation describes the diffusion process of light specific intensity $I(r, t)$ and it can be derived from heuristic arguments based on Boltzmann's classical transport theory.^[365] The diffusion coefficient D can

be obtained in this way and corresponds to $\frac{v \ell_t}{3}$, where v is the averaged speed of the electromagnetic energy in the medium and ℓ_t is the transport mean free path. This latter magnitude represents the averaged distance travelled by light before direction is randomized. Essentially the first term in the right-hand side of equation (2) describes the spreading of light intensity due to scattering processes. Its second term corresponds to the energy loss in the system due to absorption, it is proportional to the specific intensity (linear process) and proportional to the quotient of the energy speed to the characteristic absorption length, which is equivalent to the averaged inverse time between two absorption events. The last term in equation (2) describes the energy released in the system by external sources. Hence expression (2) equates the temporal variation of the intensity at one point with the variations due to absorption, energy injection into the system and spreading due to scattering.

The diffusion approximation can indeed be derived through rigorous arguments arising from the consideration of averages over the microscopic electromagnetic fields,^[366] or in a more heuristic fashion.^[367,368] In fact, the simplest way to predict the

value of the energy velocity, transport mean free path and absorption length is through the use of such microscopic models, this being an open subject. In fact, the precise determination of energy speed in active, dense and resonant media is still missing.^[369] On the other hand the diffusion approximation is not valid when the size of the system is comparable to the transport mean free path.^[370] The selection of the appropriate boundary conditions to the diffusion equation is not a trivial task.^[371] Generally the diffuse intensity $I(r, t)$ is considered to vanish at a virtual interface placed (outside the system considered) at a distance comparable to l_t . This distance is called the extrapolation length,^[366] and it is difficult to determine for more complex diffusion like in presence of scattering anisotropy.^[372]

6.2. Photonic Ohm's Law

From the solutions to the diffusion equation in the stationary regime for a slab geometry, the transmitted flux through the slab can be obtained. The resulting total transmission is governed by the photonic Ohm's law: the transmission is proportional to the transport mean free path and inversely proportional to the system thickness:^[373] $T \simeq \frac{l_t}{L}$, where L is the thickness of the system for a slab geometry which thickness is much larger than l_t .

The scattering strength of a material can be probed by total transmission measurements, via the use of an integrating sphere technique^[374] as depicted in **Figure 11a**. At variance with backscattering experiments, Ohm's law requires the study of the total transmission probability through the sample, integrated over all exiting angles, for different sample thicknesses. Ohm's law describes diffusive transport and hence a decrease of transmission with sample thickness as $1/L$.^[375] A simple fit, taking into account the average reflectivity of the sample, can then provide the value of the transport mean free path, at all wavelengths.^[211]

6.3. Dynamics of Diffusion

In the steady state, as shown in the previous section, the only magnitude governing transport is l_t . In a dynamical measurement instead, transient effects may become important. The diffusion constant D is a dynamical quantity and therefore can be probed directly with a measurement of the spread in time of a short pulse crossing the sample.^[376] For long times the pulse spread is exponential, $\sim \exp(-t/\tau)$, with a time constant given by: $\tau(\lambda) = \frac{(L+2z_c)^2}{\pi^2 D}$.

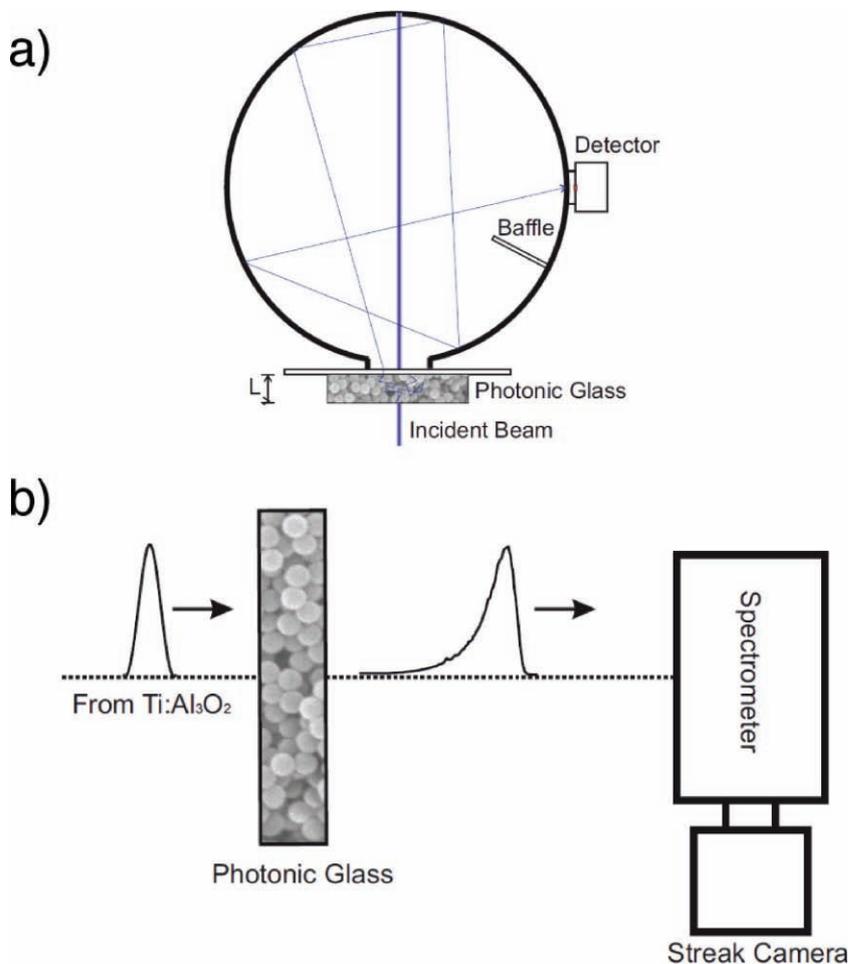


Figure 11. Light diffusion. Panel a): experimental set up to perform static measurements. A slab of photonic glass with thickness L is placed at the entrance of an integrating sphere and illuminated with white light. Diffuse light is measured at the detector. Panel b): experimental set up to perform dynamical measurements. A ultrashort laser pulse is sent to the sample. A spectrometer collects the pulse temporally spread by the sample and sends it to a streak camera.

Dynamical transport studies are complementary to the previous static analysis as they allow probing important quantities such as the diffusion constant or the energy velocity.

Due to the much faster time scale of the signal in reflection (most of the intensity is delayed only few fs), a dynamical experiment in transmission is much more feasible. Time-resolved transmission has been investigated with several types of setups, based on large bandwidth either with short light pulses or tunable laser light. The diffusion constant is usually measured from time-of flight experiments lasers as shown in **Figure 11b**.^[308,377,378] Alternatively, interferometric methods can be very efficient, especially for thin samples.^[379]

Combined measurement of D and l_t open the possibility to measure the energy velocity v as computed from the simple expression $v = 3D/l_t$.^[211] The energy velocity, given by the ratio of the energy flux to the energy density, which takes into account possibly very strong delay by resonant scattering is the most important velocity that can be defined in a disordered system in which there is no translational symmetry, the k -vector is not well defined, and, hence, neither is the phase nor group velocity.

6.4. Beyond the Diffusion Equation: Multiple Scattering of Waves

Although the diffusion approximation provides valuable information about the multiple scattering process of light in a disordered medium, it neglects relevant aspects of the wave nature of light. In particular, interference effects are neglected in this approximation.

The diffraction pattern created when light passes through a PC can be considered as built up of a set of interfering waves. Only at the directions where the superposition of waves is constructive, a diffraction spot is found. This diffraction pattern is well defined and predictable and depends on the structure of the crystal as illustrated in Figure 4b.

In the same way, light passing through a disordered sample can be regarded as a superposition of multiply scattered waves. Hence an interference pattern is also obtained. In contrast with the diffraction pattern of a PC, the one created by a disordered medium is typically composed of a disordered set of speckle spots whose statistical properties depend on the microscopic properties of the material (Figure 4c). These patterns are widely known as speckle patterns.^[380]

If one includes the full wave nature of light to the multiple scattering process, subtle differences with pure diffusion arise, which, in turn, enables the appearance of new physical effects. Perhaps the most relevant are the appearance of speckle patterns, enhanced coherent backscattering and eventually Anderson localization.

Before going into a detailed description of these phenomena, it is worth mentioning the alternative theoretical approaches that have been developed to model multiple scattering of waves without relying on the diffusion approximation. A common, and more accurate, alternative to the diffusion equation is the radiative transfer equation (RTE).^[367] RTE describes the spatial and temporal evolution of the ensemble averaged radiance in a disordered medium. The radiance describes the energy flowing towards a given direction, and at a given position and time. If the radiance is quasi-isotropic, the RTE can be approximated by the diffusion equation for the (diffuse) light intensity.^[368] An exact theory, from which RTE can be obtained, is widely known as the Bethe-Salpeter equation (BSE).^[366] It is an equation for the statistical correlations of the Green tensor in a disordered system. BSE, together with the Dyson equation, describing the averaged values of the Green tensor, provides an exact description of any second-order statistic of the electromagnetic fields in the disordered medium. In the so called ladder approximation, Dyson equation and BSE lead to RTE.^[381]

Several phenomena described in the following sections are theoretically derived from BSE perturbative diagrammatic approaches to its solution, particularly those arising from interference phenomena. The BSE can, for example, be applied to study energy transfer in disordered photonic crystals.^[382]

Extensions of the diffusion approximation, based on the so called self consistent theory of localization,^[383] allow a description of light transport near the onset of localization^[384] and its dynamical properties^[385] by considering spatio-temporal variations of the diffusion coefficient in the diffusion equation.

Random Matrix Theory (RMT)^[386] has also been used in the description of wave transport in disordered media. In

particular, it has been shown that a Fokker-Plank equation describes the evolution of the joint probability density of the scattering matrix elements as a function of the length of the disordered region.^[387,388] An important aspect of RMT-based transport theories is that these are non-perturbative, and hence they can be used to describe transport regimes where diagrammatic techniques fail, as for instance the deep localized one. A drawback of RMT is that it naturally describes quasi-one dimensional systems and hence it is not suited for open 3D geometries. We refer the reader to an introductory review on the subject.^[389]

6.5. Speckle Statistics

At a first glance, one may think that the speckle pattern, formed by the interference of multiple scattered waves in a disordered medium, is a set of randomly placed and intensity-uncorrelated spots. Far from what intuition suggests, the speckle pattern is not fully random. In fact, strong correlations are present in the speckle pattern. It has been shown, using different theoretical approaches, that the intensity correlations of light transmitted through a random medium, both angular and spatial, can be decomposed in three terms of different range, usually known as $C^{(1)}$, $C^{(2)}$, $C^{(3)}$ correlations.^[366,390–395] $C^{(1)}$ correlations correspond to short range correlations, related to the fluctuations in the intensity of one speckle spot. $C^{(2)}$ correlations are the main contribution to the intensity correlations of two separate spots of a speckle pattern. When the system is diffusive, this correlation is numerically equivalent to the fluctuations of the transmitted intensity through the system. This fact implies that intensity correlations among different spots are positive. Nevertheless, when the diffusion approach is no longer valid, this correlation can be negative.^[396] This phenomenon arises when the size of the system is comparable to the mean free path. The $C^{(3)}$ correlation is a long-range term. The intensity of spots in different speckle patterns, formed by different illumination beams, is not zero.

A delicate interplay of the different types of speckle correlations gives rise, in non absorptive random systems, to an interesting and counter-intuitive result: the fluctuations of the total transmitted power, considering all possible incident angles, are a constant irrespective on any parameter describing the system. This is known in the literature as Universal Conductance Fluctuations (UCF)^[397,398] as it was first theoretically predicted for the conductance statistics of disordered electronic systems. The optical analogue has been proven to be valid.^[399]

In the multiple scattering regime, the developed speckle pattern is built as a result of the superposition of multiply scattered waves travelling along different paths in the medium. Small modifications in the position of scatterers lead to large variations in the relative phase associated to different paths. Hence, if the scattering medium is dynamic, the dynamics of the speckle pattern, and in particular its autocorrelation time, depends on the microscopic dynamics of the system. Diffuse wave spectroscopy^[400] is a technique based on this concept, and its use permits to obtain information about dynamics of the microscopic system such as diffusion constants of the microscopic scatterers and its motion.^[401]

When the light entering the random system is not produced by external and well controlled sources such as a laser beam, but it is produced by sources immersed in the system, a new source of fluctuations in the resulting speckle pattern is found: the total power emitted by a point source is not fixed but depends on the surrounding medium through the local density of states. Hence, the statistics of the power emitted by such a source, provides a measurement of the statistics of the LDOS in the medium. The contribution to the speckle correlations due to the LDOS fluctuations is known as $C^{(0)}$ correlation.^[390,391]

Recently, a connection between the averaged values of the LDOS and the extinction mean free path has been established.^[402] Only based on causality considerations, it can be shown that both magnitudes are related through a frequency sum rule.

The phase and amplitude distributions of a speckle pattern contain important information like the local density of states^[403] while the speckle correlation, in space, angle, or frequency^[404] can provide microscopic details of the photonic structure. Intensity correlation function of the speckle pattern from disordered PC represents a sensitive tool for determination the stop-band width.^[405]

6.6. Coherent Backscattering

Among the effects arising due to the wave nature of light in multiple scattering random systems, we find the Coherent Backscattering (CBS) effect and weak localization.

When a multiply scattering medium is illuminated by a laser beam, the scattered intensity results from the interference between the amplitudes associated with the various scattering paths; for a disordered medium, the interference terms are washed out when averaged over many sample configurations, except in a narrow (milliradians) angular range around exact backscattering where the average intensity is enhanced.^[406,407] This substantial enhancement (approaching a factor of two) is called CBS cone.^[190,408] Notice that back scattering means that incoming and scattered light share the direction nearly exactly while having no relation with sample orientation. Only diffusive materials can “reflect” light back towards the illuminating source when the sample is not perpendicular to the illumination.

The same effect leads to a net reduction of light transport in the forward direction, similar to the weak localization phenomenon for electrons in disordered (semi)conductors^[193] and is often seen as the precursor to Anderson (or strong) localization of light.^[194] Nevertheless, it can be proven that suppression of weak localization does not necessarily implies absence of strong localization, for instance in systems where reciprocity symmetry is broken.^[389]

The width of the CBS cone is inversely proportional to the product $(k l_t)$, wavevector times transport mean free path, it can be effectively used to determine l_t . Experimentally, different setups for accurate large angle measurements have been proposed,^[409] techniques that approach the full 2π angle with negligible noise. These techniques can probe very short transport mean free path, down to values comparable with the light wavelength, and are therefore useful for very strongly scattering samples, like semiconductor powders. Weakly scattering media

like human skin, aerogels or nematic liquid crystals, with scattering lengths of \sim mm, require the measure of very small scattering angles, which motivated experiments that reached tens of μ rad resolution.^[410] In addition, broadband spectroscopy of the coherent backscattering is now possible,^[411] opening the possibility to study chromatic dispersion in the scattering lengths. It is known that systems in which multiple scattering is not fully developed or where reciprocity symmetry is broken, for example in a magnetic active medium, weak localization and CBS is suppressed.^[412]

The main practical difference between backscattering and transmission experiments is in the surfaces crossed by light, *i.e.*, the boundary conditions. Backscattering experiments are very much affected by the quality of the sample surface, and the majority of the signal and noise comes from a volume close to the first surface, even if the results obtained are independent on sample thickness. Transmission measurements are usually more sensitive on both the sample surfaces and on its thickness but the signal and noise come from a much larger volume, making the measurement less sensitive to imperfections on the sample front face, but more on its bulk.

6.7. Anderson Localization

Anderson localization was predicted for electrons by Philip Anderson in 1958,^[194] for which he won the Nobel prize in 1977. In a one-dimensional disordered system, the eigenstates corresponding to the single electron Hamiltonian present a finite spatial extension, even when the energy of eigenstates is higher than the potential barriers of the system, in other words, electrons can become localized not due to energy confinement, but due to the interference of multiply scattered (matter) waves.

Anderson localization, also known as strong localization, is the absence of diffusion of waves in a random medium, and can be studied for photons^[194] as well as for electrons. It is a phenomenon that relies on wave interference, and therefore it is general to any wave system in nature, and specifically to light – electromagnetic waves. Seen for many years as one of the holy grails of the photonic science, and predicted to occur more easily in random but correlated media like disordered PCs,^[4] it has been very recently reported for disordered 2D periodic structures^[413] and for strongly scattering TiO_2 powders.^[378]

In three dimensions, localization is expected to happen if the mean free path is comparable to the wavelength. More specifically if $kl \leq 1$, l being the (elastic) mean free path and k the wavenumber, condition that is known as the Ioffe-Regel criterion.^[414]

Wave transport in the localized regime shows different statistical properties from usual diffusive transport. In particular the diffusion approximation is no longer applicable. Ohm's law is not valid in this regime, the transmission of the disordered system being an exponentially decaying function of the length of the disordered system rather than linear, although this dependence may be masked by absorption losses in the system. In fact, the vanishing of the diffusion constant is considered a stronger proof of Anderson localization than an exponentially decaying total transmission.

So far, the most studied self-assembled random medium for light localization has been strongly scattering titanium dioxide powder, for its ease of fabrication, high refractive index (~ 2.8) and strong scattering, with $l_t \sim 0.1\text{--}1\ \mu\text{m}$. In 1997 scale-dependent diffusion constant was deduced from transmission experiments in gallium arsenide powders,^[198] and later in 2006 time-resolved experiments on similar samples have observed surprisingly large decay times of the energy stored in the sample.^[378]

At present the experimental search for Anderson localization in 3D disordered systems is still an active research field. We refer the reader to several review articles on the subject.^[407,415–418]

6.8. Random Lasing

Fascinating phenomena can take place when optical gain is added to a random medium. For high enough optical gain light fluorescence can be amplified by stimulated emission up to a level that lasing can occur. This is the so-called random lasing and it is a special form of lasing which takes place in disordered materials with gain, where multiple scattering of light provides the “feedback” to make gain larger than losses and reach gain saturation, the fundamental mechanism that leads to coherence.^[419] Initially predicted by Lethokov in 1967,^[420] random lasing has been demonstrated 20 years later,^[204,421] and it is still a very active research field.^[422]

Multiple scattering increases the interaction between light and the system, and, if gain is added to this scenario, the system, eventually, lases when stimulated emission dominates over the spontaneous emission of light. No mirrors are needed in a random laser to reach laser action and light scattering, which is generally regarded as a parameter to minimize in standard lasers, is the *sine qua non* condition to observe the effect. Standard random lasers output properties are fixed a priori by the gain medium and the emission wavelength, for example, is determined by the maximum of the gain curve. In **Figure 12** the typical behaviour of a random laser system is shown.^[423]

Active photonic glasses have been shown^[212] to open a route to exert a control over the lasing parameters through the material nanostructure itself and to control the laser output. Due to the monodispersity of the scatterers, the resonant behaviour in the diffuse light through a photonic glass allows controlling the laser emission via the diameter of the spheres and their refractive index. Such a system is a dispersive random device with a priori design lasing peak within the gain curve.^[212,424]

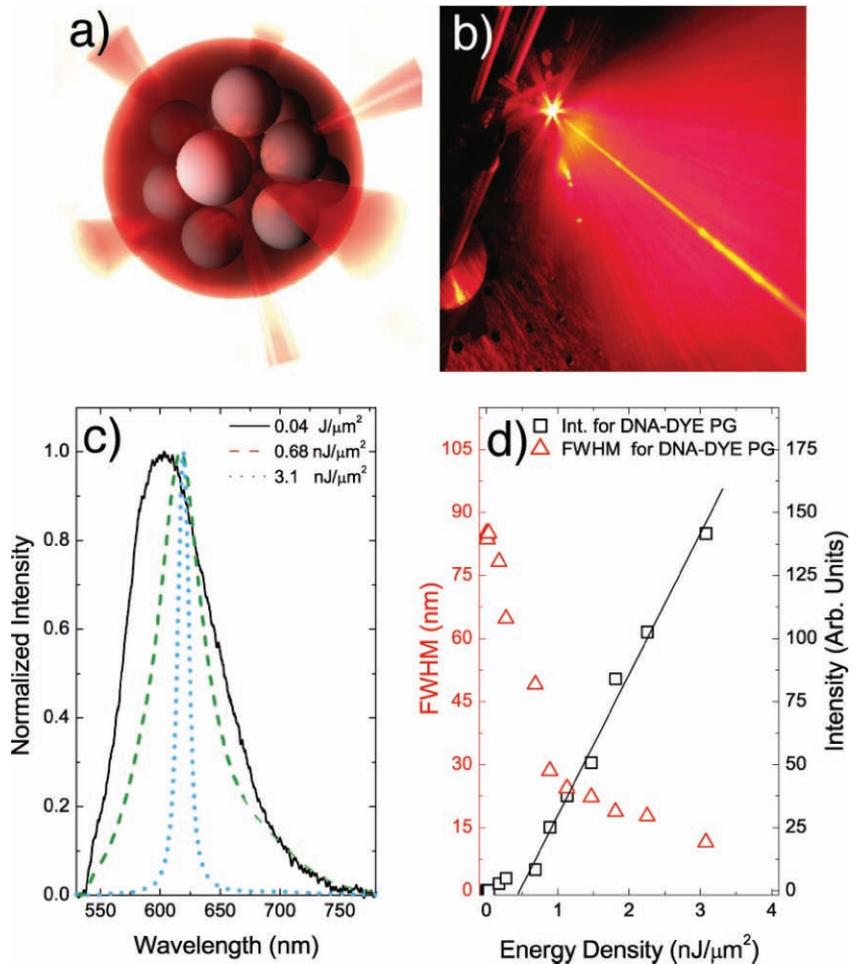


Figure 12. Random lasing. Panel a) shows an illustration of the random lasing process in photonic glasses doped with DCM laser dye. A green laser pump excite the dye molecules that fluoresce starting a cascade process that lead to stimulated emission and lasing. Panel b) shows a real image of the random lasing. Panel c) Emission spectra from DNA-DCM infiltrated photonic glass at different pump power, below and above the random lasing threshold. Panel d) Emission maximum (empty squares) and full width at half maximum (empty triangles) as a function of pump energy for a Photonic Glass infiltrated with DNA-DCM and with the same quantity of dye (filled circles) plotted. Continuous line results from a linear fit of the points above threshold. Panels c) and d) Reproduced with permission.^[423]

6.9. Non-Random Disordered Media: Disorder in Photonic Crystals

While the phenomena described so far hold for fully random media, with no positional or size correlation of their constituents, they can effectively be extended to other type of disordered media. The optics of disordered but not random media is a fascinating realm which has just started been unveiled. The full potentiality of 3D fractal,^[181] quasiperiodic,^[182,183] or correlated media^[205] has still to be explored.

The physics of light transport and scattering from photonic crystal is very rich and interesting, and has been explored since the first years of the photonic crystals development.^[425] Further, the presence of disorder has severe implications in the optical performance of opal-based photonic crystals, from the introduction of propagation losses^[426] to the possibility of a

complete closing of the full PBG,^[427] which could hamper future applications.

Light scattering by weak topological disorder in a 3D PC is determined by the interplay between order and disorder. Even in the highest quality PCs intrinsic disorder triggers light scattering that, for thick enough crystals, provokes that ballistic transport of light is replaced by diffusion. Motivated by the search for better photonic crystals much research has been devoted to understanding the scattering losses and the process of single scattering in opals. For instance, angular-resolved spectroscopy on photonic crystals have probed the link between light scattering and the photonic bands,^[294,428,429] and speckle studies have helped unveiling the properties of the photonic bandgap.^[405]

The full potentiality of periodic photonic materials can be seen in the way they alter diffusive light transport and multiple scattering. For sufficiently weak disorder the diffusion limit in disordered photonic crystals can be expected, as calculated by RTE.^[382] Diffuse light is expected to undergo the same phenomena as ballistic propagation, namely, being affected by the special dispersion characteristics of Bloch modes. Single scattering events in a system with modified light modes and density of states, as in a PC, are very different from those occurring in vacuum due to: a) an increase of light-matter interaction and thus of scattering by defects, when the $DOS(\omega)$ is increased at the vicinity of band-edges and b) a suppression of the scattering channels, *i.e.* an increase of l_s in the band-gap, where $DOS(\omega)$ is strongly reduced.

As pointed out by John,^[4] a dramatic change in light diffusion can occur for frequencies in or around the band-gap and eventually Anderson localization of light can be reached, the photonic conductor becoming an insulator. In the quest for light localization, the first experiments focused on fully random media^[198,378,430] and only recently transverse localization has been reported in two-dimensional crystals with disorder.^[413]

Even far from the localization regime, the scattering properties of Bloch modes, the periodic electromagnetic modes of a PC, are expected to be profoundly different from the diffusive modes encountered in conventional random media. Pioneering experiments on coherent backscattering^[431,432] and diffuse light transport^[433] in PCs have been searching for signatures of Bloch-mode mediated scattering but have merely shown standard light diffusion. Moreover, the experiments have been interpreted using a model that assumes no photonic modal dispersion,^[426] but rather a modified reflectivity at the system boundaries. In a similar framework, enhanced scattering and dispersion have been observed in carbon-doped PCs.^[434] Only recently the role of the modified density of states on light scattering have been pointed out.^[307]

As shown in this chapter the building block for a multiple scattering picture is the scattering mean free path (l_s). By means of Lambert-Beer law strong chromatic dispersion of l_s has been reported (Figure 13) and values of up to ~ 100 – 500 μm , that is to say ~ 300 times the lattice parameter.^[431] Large l_s and in particular a scattering length bigger than the Bragg length (l_B) but smaller than the system size (L) is the first requirement for a study of multiple scattering in photonic crystals: $l_B < l_s < L$. If l_s was larger than l_B than the photonic crystal would behave like an ordinary random medium, while if l_s was larger than L

than the probability for more than single scattering would be negligible.

In parallel to a large variation of the single scattering parameters, also an extraordinary reduction of the diffusion constant has been observed in partially disordered silicon inverted photonic crystals,^[308] where diffusion is even stronger than in an equivalent random media.

Despite all these very important advances, the study of diffusive light transport in 3D photonic is still a field open to new discoveries, as for example the proof of bandgap-disorder induced Anderson localization of light or evidence of lasing from localized states in photonic crystals^[435] are still awaited but missing.

7. Functionalities

The peculiar way in which self assembled nanostructured materials interact with light makes them a promising platform for a number of applications in the field of photonics as pointed out by recent literature.^[436–438] Though in many cases the performance of the system has not yet achieved the state of the art of current technology, proof of principle has been demonstrated for several applications. As mentioned in Section 4.2, controlled defects of different dimensionalities have been introduced in artificial opals which could find future applications as parts of photonic integrated circuits such as wave-guides, active cavities for lasing, etc. Efficient light emitters such as lasers (see Sections 5 and 6) or even “cold light sources” could also benefit from self assembled PCs. In the later, thermal emission is customized by means of Bragg diffraction and absorption to suppress long wavelength components, and obtain more efficient light sources.^[439–441] In this section, other possible applications for self assembled structures are described.

7.1. Tuning

While PCs based on self assembled materials are of interest for a number of applications, their functionalities can be certainly enhanced if one can modify their optical properties in real time under an external stimulus turning them into tunable devices. In order to tune the optical response of these materials, one can either modify its topology or the refractive index of its components, both being factors determining their dispersion relation and hence their optical performance. The applicability of such tuning process will depend on whether the modification of the optical response takes place in a non-reversible way (more appropriate for fine tuning in the fabrication process) or in a reversible one (ideal for truly tunable devices). Even if the tuning process takes place in a reversible way, one has to consider its time scale, since it will determine the applications which can be envisaged (such as sensors, optical memories, etc.). A number of strategies have been presented over the past years to fabricate tunable structures exploring different materials and external stimuli.

The first approach was presented by Asher and co-workers^[442] who explored mechanochromic PCs whose spectral response could be modified by applying an external

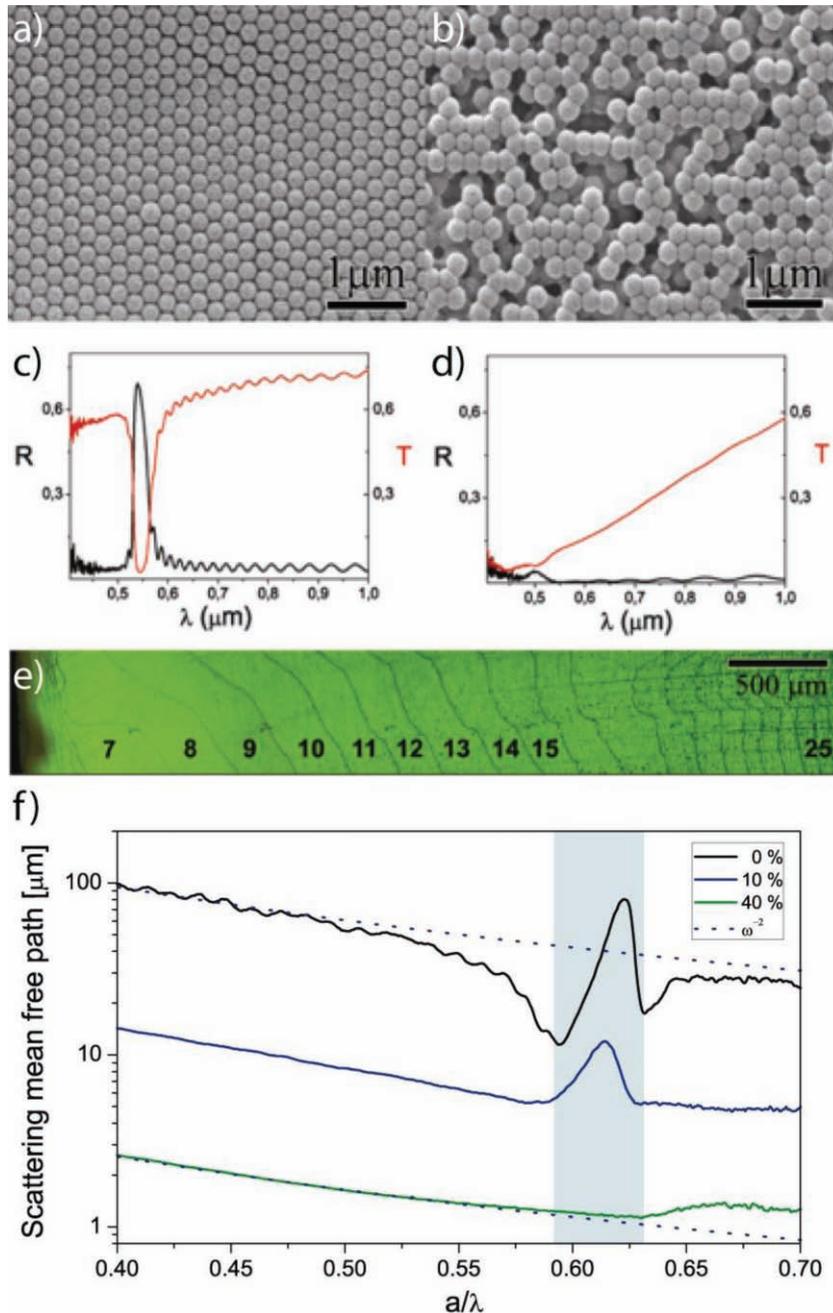


Figure 13. Disorder in PCs. Top panels shows SEM images of PC with 0% (a) and 40% (b) vacancy doping. The middle panels (c) and (d) show the reflection and transmission measured from the corresponding samples of the above panel. On the panel (e) an image from an optical microscope of the opal surface, in which the different layers are distinguishable as terraces and numbered. Panel (f) shows the measured l_s in the PC over the value measured in the pass band (which is the expected l_s value for the effective medium without photonic features) Reproduced with permission.^[307]

strain on the sample. In their case they studied a composite crystal obtained by locking a periodic array of polymeric colloidal particles in a hydrogel matrix. By applying a uniaxial strain in the plane parallel to the sample surface, the distance between (111) planes is modified, and hence the spectral position of the pseudogap shifts in a reversible manner. Several subsequent

studies on mechanochromic samples^[443] have extended this idea achieving a larger spectral shift of the pseudogap,^[444] studying different types of samples such as polymeric artificial opals^[445] or inverse opals^[446] and fabricating samples whose mechanochromic response is able to follow fast (200 Hz) stimuli.^[447] By changing the sample topology under an external stress/strain one can aim not only at changing the optical response of the material, but also at controlling the emission of internal sources,^[448,449] leading to tunable lasers.^[364] Also exploiting the mechanochromic response of elastomeric inverse opals, a biometric recognition device has been proposed whose optical response changes locally under the pressure of a fingertip, revealing the fingerprint.^[449]

Of special interest for all-optical applications are photo-tunable materials whose refractive index or structural properties can be modified when exposed to an external control light beam. After initial experiments where the lattice parameter of a periodic array of SiO₂ beads embedded in a monomer matrix was modified in a non reversible way by a photopolymerization process,^[443] several strategies have been followed. Introducing a photoionizable molecule in a colloidal crystal, the ion concentration in the solution could be altered by illuminating the sample with UV light which leads to a transition between ordered and disordered phases, modifying the optical response of the sample.^[450] An alternative approach has been explored exploiting the photoisomerization of photochromic molecules to tune the optical properties of self assembled PCs. The later was done either relying on refractive index changes associated with the formation of molecular aggregates^[451] or the volume changes experienced by hydrogel matrices to which azobenzene derivatives were covalently attached.^[452] Based on these systems the possibility of developing optical memories has been proposed. If the induced change in the optical response is durable enough, one could “write” and “erase” information in the system by using different wavelengths and “read” it by detecting the Bragg diffracted light.^[453]

Different routes have also been followed to employ temperature as the external stimulus to tune the optical properties of self assembled PCs. Weissman *et al.* employed the temperature induced volume phase transition of PNIPAM to change the optical response of self assembled colloidal crystals.^[454] They fabricated both, ordered suspensions of PNIPAM spheres in water and arrays of polymeric particles in a PNIPAM matrix. In the former, the scattering cross section of the spheres could be temperature

controlled creating a crystal whose Bragg diffraction could be switched on/off, while in the latter volume changes varied the lattice parameter of the structure continuously tuning the wavelength of the Bragg peak associated with the pseudogap. Also, the optical response of macroporous hydrogels has been tuned across the visible with temperature as the external stimulus.^[455]

Incorporating azobenzene units into the gel, and turning it photochromic, it was possible to combine a continuous temperature-driven tuning with an on/off photo-driven mechanism^[456] adding versatility to the system. In a different approach an inverse opal was made from a ferroelectric material (BaTiO₃) and, changing the temperature in the surroundings of the phase transition point, induced changes in refractive index which spectrally shifted the pseudogap of the sample.^[457] Artificial opals built from semiconducting Se-Ag₂Se core-shell colloidal particles have also been demonstrated as thermally tunable PCs.^[65] Changing the temperature in the surroundings of the α -Se to t -Se and β -Ag₂Se to α -Ag₂Se phase transitions induced changes in refractive index which translated in spectral shifts of reflection peaks. More complex architectures, such as artificial opals with thermally (and photo-) isomerizable planar defects have been presented^[458] which could find use as tunable optical filters. Finally, VO₂-SiO₂ opals have been recently fabricated where the spectral position of the Bragg peak, located at 1.55 μm , was tuned by changing the temperature across the metal-semiconductor transition temperature of VO₂.^[459]

When dealing with dynamically tuning the optical properties of PCs, liquid crystals (LCs) have been one of the most popular materials ever since the first theoretical proposal for its use as a means to open/close the full PBG of an inverse opal filled with them.^[460] Their attractiveness comes both from their optical anisotropy providing a tunable refractive index, dictated by the orientation of the LC molecules, and the possibility of easily introducing them into the porous matrices of self assembled PCs. The versatility of tunable LC-filled PCs has been demonstrated in a number of systems including both direct and inverse opals using different external stimuli. Yoshino *et al.* carried out initial experiments where the optical properties of artificial opals infiltrated with nematic and smectic LCs were thermally tuned when moving around the phase transition temperature.^[461] Thermally controlled phase transitions have also been explored in inverse opals by Mertens *et al.*^[462] Using external electric fields to orient the LC molecules in a PC matrix could open the way to build tunable electro-optic devices. Nematic LCs were infiltrated in artificial opals and its optical response studied under an external field, finding a faster reorientation of the LC molecules than in a conventional electro-optic device.^[463] Later, the effect of molecule orientation with respect to the sphere surface was also studied in a similar system.^[464] Inverse opals have also been studied as tunable electro-optic devices, employing dual-frequency LCs which permits increasing the tunability range of the device.^[465] Inverse opal films filled with LC molecules with incorporated azobencenes have been employed to tune the optical response of the system orienting the LC molecules by means of an external light beam,^[466] and even using two external stimuli simultaneously –light beams and electric fields– to achieve higher control on the optical response of the sample.^[467] The complex behavior of liquid crystal molecules when located in a structured porous environment has to be

taken into account in order to understand many of the observed phenomena in the above systems. The role of the connectivity of the porous network in the response of the liquid crystal molecules^[468] or the strong dependence of anchoring effects with surface treatment^[469] have been studied in these structures.

Finally, electric and magnetic fields have also been used as a means to tune the optical properties of self assembled PC with different components. Tunable self assembled PCs were made from ferroelectric ceramics whose refractive index was changed under an applied electric field.^[470] In a different configuration, mechanochromic PCs were placed between two flexible electrodes whose separation was controlled via an applied high voltage bias, changing in this way the separation between crystallographic planes parallel to the sample surface and hence its optical response.^[471] Arsenault *et al.*^[472] fabricated a continuously tunable full-colour digital display. In this work, they immersed a SiO₂ opal filled with a metallopolymer in an electrochemical cell. By applying an external voltage, oxidation/reduction processes were induced which allowed controlling in a continuous manner the sample lattice parameter and hence its reflection band. This approach was later improved with an inverse-opal configuration,^[473] where the SiO₂ scaffold is removed, and a better flow of the electrolyte allowed faster tuning speed and lower applied voltages.

Magnetic fields were also used to tune the optical response of self assembled PCs. If a colloidal crystal formed by superparamagnetic colloidal particles (containing Fe₃O₄) is placed in a region where an inhomogeneous magnetic field is being applied, the crystal will be compressed along the direction of the magnetic field gradient, and its forbidden frequency band will blue shift in a reversible manner.^[474,475] A different approach in the search for a magnetically controllable PC has been the fabrication of a ferromagnetic inverse opal which, when placed in water, can be physically rotated in the presence of an external magnetic field, opening the way for optical MEMS devices.^[476]

7.2. Sensors

Over the past decade, much attention has been devoted to the use of self assembled PCs as sensors. For this purpose one needs only to fabricate a system whose refractive index or topology, and hence optical response, changes in the presence of the external stimulus which one wishes to detect, much like the working principle of the above mentioned tunable devices. Asher and coworkers^[477] published in 1997 a seminal work in which a PC formed by a periodic array of polystyrene spheres in a hydrogel matrix was turned into a sensor by adding molecular recognition agents to the hydrogel. The matrix would experience a volume change in the presence of certain analytes –metallic ions or glucose in this case– as a consequence of a change in osmotic pressure, varying the lattice parameter of the PC and thus its optical properties would be modified accordingly. This working principle is illustrated in **Figure 14**, as extracted from ref.^[478]. The magnitude of the change in the optical response depended on the analyte concentration and could be perceived even by the naked eye. This approach has been thoroughly used in subsequent years by Asher's and several other research groups, either employing the polymer/hydrogel composite

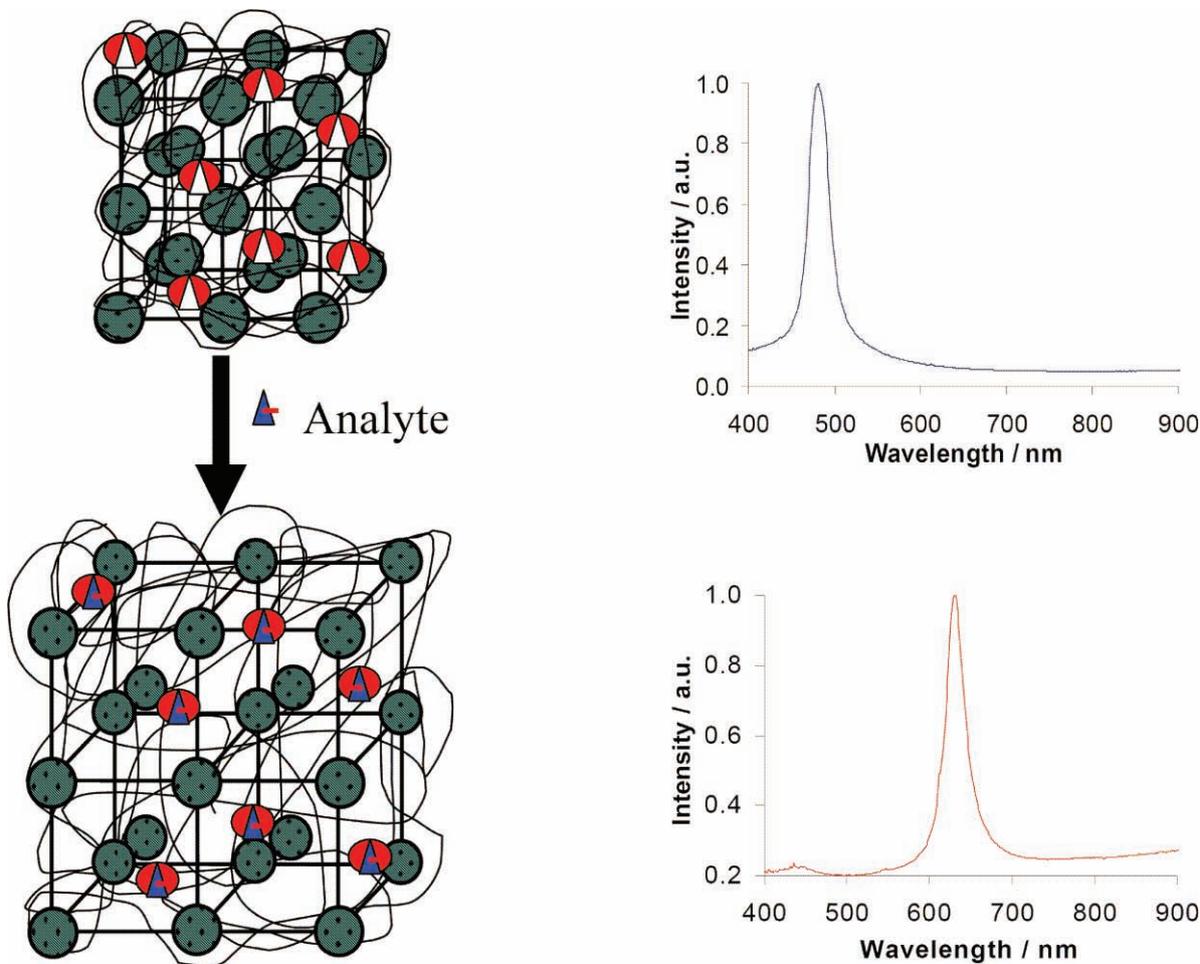


Figure 14. Working principle of polymerized crystalline colloidal array PC sensors. (Top) A colloidal crystal (green spheres) is surrounded by a hydrogel (black line) containing a molecular recognition agent (red spheres containing blank triangles). (Bottom) In the presence of a certain analyte (blue triangle) which interacts with the molecular recognition agent, the hydrogel undergoes a volume change which causes a shift in the frequency being diffracted by the PC, causing a change in the sample macroscopic color. Reproduced with permission.^[478]

system or other forms of periodic self-assembled structures such as direct or inverse opals. Sensors for glucose,^[479] pH,^[480] ionic strength,^[481] biological agents,^[482,483] organic vapors,^[484] or humidity^[485] to name a few, have been developed over the past few years. Beyond presenting a proof of principle, in some cases the fabricated sensors were proved to function in environments with high ionic strength – as is the case of biologic fluids – and able to detect physiologically relevant concentrations, hence ideal for direct applications as real-life bio-sensing devices.^[486,487]

Following the principle of these chemically tunable PCs the so-called “photonic papers” and “photonic inks” have been proposed (see **Figure 15**). Here the optical properties of a PC are modified locally by applying organic solvents to periodic arrays of polystyrene spheres in a matrix made of elastomer.^[488] Where the solvent acting as “ink” is applied, a change in matrix volume causes a spectral shift of the Bragg peak which produces an appreciable change of color in the sample. Further developments in photonic papers have led to permanent writing by photopolymerization of locally applied monomers^[489] and rewritable devices where hygroscopic salts are used as inks in composite opal based crystals.^[490]

7.3. Switching

If in the future optical integrated circuit components are to be fabricated from self assembled materials, all optical switching lying at the heart of logical processing will be a must. In this direction, a number of publications have appeared over the past few years demonstrating the feasibility of switching the optical properties of artificial opal based PCs in very short times. In particular, much attention has been devoted to realizing the switching process all-optically, ideal for the photonic integrated circuit scenario.

Initial tests studied switching in low refractive index contrast polymeric colloidal crystals.^[491] Starting from index-matched self assembled structures of dye doped colloidal particles in a hydrogel matrix, an intense excitation pulse was absorbed by the dye, heating the spheres and creating a refractive index contrast which caused the structure to diffract light in a nanosecond timescale. Later, the attention moved towards more strongly photonic structures and faster switching times. The spectral position of the Bragg peak in polystyrene opals was switched in a picosecond^[492] and subpicosecond^[493] time scale. The change

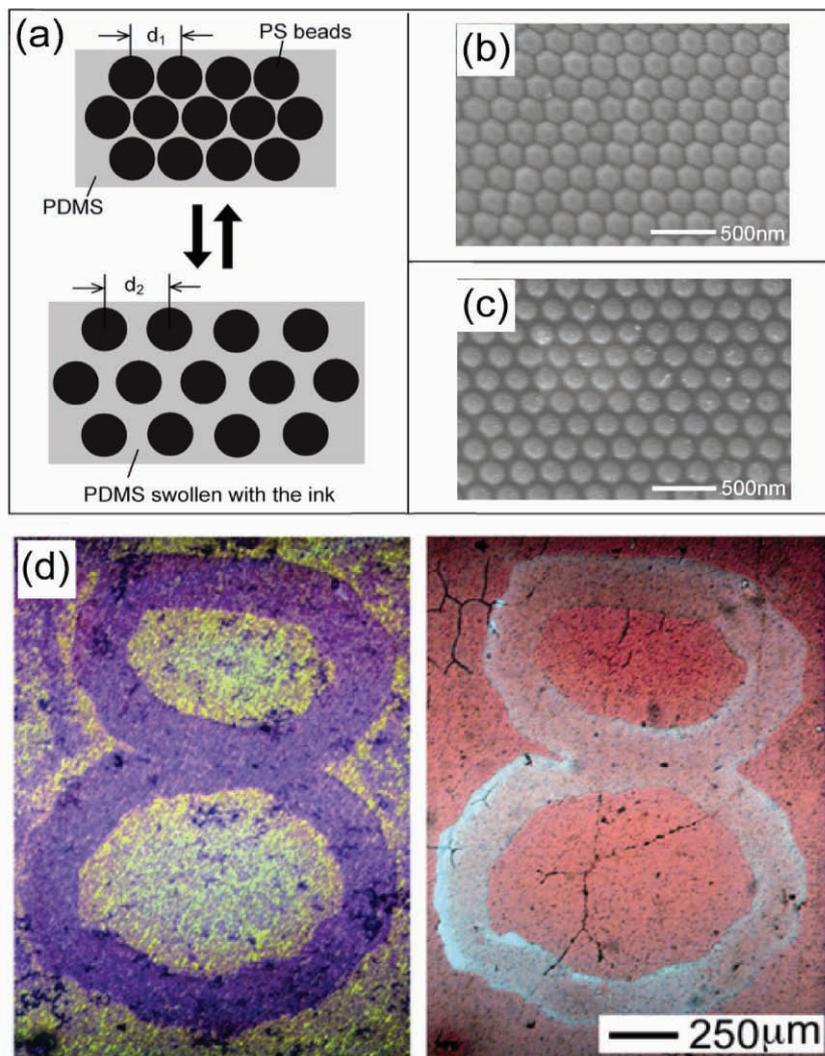


Figure 15. Schematic illustration of the process of writing on a “photonic paper”. (a) Diagram of a polystyrene artificial opal embedded in a PDMS matrix. “Writing” and “erasing” is achieved by adding and evaporating an “ink” (typically an organic solvent) which swells the PDMS, producing a change in the lattice parameter and hence in the diffracted frequency. (b) and (c) are SEM images of the composite material in the un-swollen (blank) and swollen (written) states. (d) Optical microscopy images in reflection (left) and transmission (right) of a photonic paper on which the figure of 8 was written. Adapted from [488].

in refractive index was here obtained by the optical Kerr effect under intense pulsed excitation. An ultrafast modification of the optical response of VO₂ infiltrated opals was attained by photo-inducing a semiconductor-metal phase transition under pulsed laser excitation.^[494] Recent advances have focused on silicon PCs with high refractive index contrast. Mazurenko *et al.*^[495] studied the spectral shift and time evolution of the Bragg peak of SiO₂-Si composite opals in the subpicosecond regime changing the silicon matrix refractive index by means of free carrier injection. Silicon inverse opals have recently been studied where the optical response in the surroundings of the pseudogap^[496] and the full PBG (see **Figure 16**)^[497] were switched in a picosecond timescale. In both cases free carriers generated by two-photon absorption processes were responsible for the large refractive index changes attained (of the order of a few percent).

7.4. Enhanced Light-Matter Interaction

The dispersion relation of a PC presents spectral regions where energy bands have a small slope, mainly for wave vectors near the Brillouin zone edge and for high frequencies where Bragg diffraction by several families of planes takes place. Light coupling to these bands is known to undergo a stronger interaction with the PC due to a reduction in the associated group velocity, as mentioned in Section 5. By exploiting these dispersionless bands PCs have been used as a mean to obtain effects based on this enhancement.

Beside applications regarding optically active media for light generation, as mentioned above, regions of reduced group velocity have also been employed to enhance the non linear response of composite opals. For example enhanced second harmonic generation was measured for silicon-SiO₂^[498] and YIG-SiO₂ composite opals.^[499] This enhanced SHG has been recently measured in polystyrene artificial opals, where the spheres were coated with a non linear molecule.^[500]

Similar effects have also been exploited in 3D opal based PCs having magnetic components. Pavlov *et al.*^[501] studied artificial opals with their pores filled with magnetite Fe₃O₄ particles and observed an enhanced magneto-optical Kerr effect at the pseudogap low energy edge which they associated with the low v_g experienced by light. An enhanced Faraday rotation had been previously measured in a colloidal crystal impregnated with a transparent liquid with a high Verdet constant, although in that case the exact mechanism of enhancement was not unveiled.^[502]

Other applications have used low v_g spectral regions to amplify light absorption. A clear example of this is the use of self-assembled PCs to enhance light harvesting efficiency (LHE) in dye sensitized solar cells. Malouk and coworkers were the first to claim

an enhanced LHE for dye sensitized solar cells containing TiO₂ inverse opals,^[503,504] though the effects they observed where later claimed to originate at resonances localized at the sample surface.^[505] Recently,^[506] experimental evidence for enhanced LHE due to reduced group velocity at the pseudogap edge was presented in samples similar to those of reference.^[499] Other proposals to obtain enhanced LHE, though not based on reduced group velocity but rather on multiple scattering of light, were presented in the form of “photonic sponges”^[507] and hierarchically structured ZnO films.^[508] In both cases efficient multiple scattering is obtained by combining colloidal particles of different diameters. Also of interest for silicon based solar cells is the use of semiconductor films in contact with artificial opals where the photoconductivity of the former can be enhanced by the combined effect of resonant modes at the film due to the

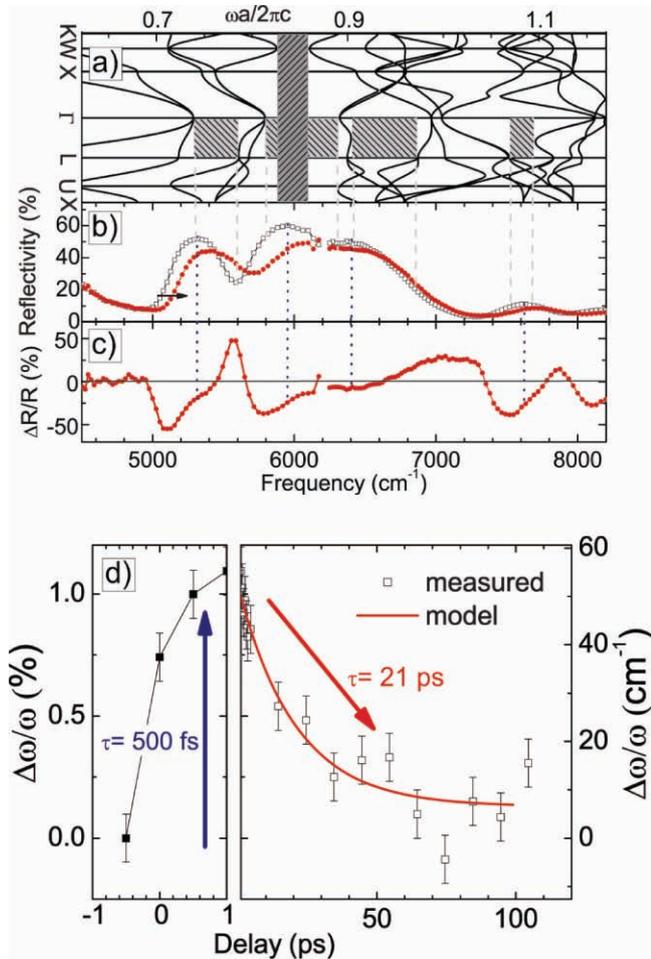


Figure 16. Ultrafast switching in a silicon inverse opal. (a) Band structure of the inverse opal in the absence of optical pumping. Light grey areas correspond to pseudogaps along the Γ L direction, and the dark grey area indicates the full PBG. (b) Reflection spectrum of the unswitched (open squares) and switched (filled circles) sample. (c) Differential reflectivity spectrum between the switched and unswitched states. (d) Temporal evolution of the blue shift of the low energy edge of the first pseudogap (region I in figure a). Left panel shows the evolution during the pumping and the right panel corresponds to the exponential decay once the optical pumping is turned off. Adapted from [497].

presence of the opal pseudogap as well as modes coming from diffraction by the 2D periodicity of the opal surface.^[509]

Recently, the use of increased absorption due to slow photons in photochemical processes has also been studied,^[510] for example matching the absorption band of TiO_2 with the pseudogap edge of a dye coated TiO_2 inverse opal to amplify the dye's photodegradation. This approach was further improved by placing Pt nanoparticles on the PC surface, enhancing the separation between the UV excited electron and holes.^[511]

7.5. Anomalous Dispersion

The real part of the effective refractive index of a finite self assembled PC undergoes anomalous dispersion across the pseudogap frequencies, similar to the case of 1D PCs.^[512] In this

spectral range, the index of refraction decreases with frequency, at variance with conventional transparent materials. These circumstances allow obtaining phase matching conditions, where the index of refraction of the material at a given fundamental frequency and its multiples are equal, which is essential when pursuing efficient second or third harmonic generation.

This dispersive behaviour was first exploited in 3D self assembled PCs to obtain second harmonic generation in centrosymmetric materials consisting of a colloidal crystal formed by polymer beads with an organic dye on its surface.^[513] In this system, inversion symmetry was broken at the sphere surface and phase matching was achieved via the anomalous dispersion of the 3D structure. In a similar way, Boyd and coworkers obtained enhanced third harmonic generation in polystyrene opals.^[514]

7.6. Other Applications

Many applications for self assembled materials like those mentioned in the previous sections have been proposed in recent years which do not deal directly with their optical properties. In this section, a brief account of the most popular ones is given.

The natural tendency of monodisperse colloidal particles to self assemble, under the appropriate conditions, into 2D periodic arrays on a substrate was first used in 1982 by Deckman *et al.*^[515] to develop what they called "natural lithography". In their work, the 2D porous array was used as an inexpensive and facile lithographic mask to fabricate 2D textured surfaces by means of reactive ion milling on silicon substrates or evaporation of silver. Such 2D arrays are useful for several applications from surface enhanced Raman scattering (SERS), to optical gratings, sensors, anti-reflection coatings, etc. Since the original work by Deckman a number of variations of the method have been developed.^[516] Combining the 2D colloidal arrays with different post-processing techniques such as sputtering, electrochemical deposition, chemical vapour deposition, etc. several 2D structures have been fabricated including nanopillars, pore arrays, nanorings, etc.

Deposition of 2D arrays of colloidal particles can be employed not only as lithographic masks but also as a low-cost approach to fabricate microlens arrays for improving the extraction efficiency of LEDs. By placing a monolayer of SiO_2 layers attached by means of a thin PS film to a light emitting diode made from InGaAs quantum wells the integrated PL from the device was seen to increase by *ca.* 300%. Such improvement in the performance of the device was attributed to both, a reduction in reflection at the light emitting diode/air interface and an enhanced photon escape cone.^[517]

Besides the above mentioned approaches, other strategies have been followed in order to design sensors based on self assembled materials. Metals, which are usually avoided in photonic applications due to their absorptive properties in the visible, have proved useful for sensing purposes. Tessier *et al.*^[518] demonstrated how one could exploit the high porosity present in inverse opals for SERS, profiting from larger contact areas and efficient analyte transport. Metallic inverse opals made from gold nanoparticles were shown to present a SERS performance similar to that of 2D silver gratings produced by lithography, with the additional advantage of an easier and inexpensive

fabrication method.^[519] Also exploiting the high porosity of self assembled structures applications for gas sensors^[520] and catalysis have been demonstrated.

Finally, exploiting the morphology of self-assembled systems and the possibility to structure its surface with a fine degree of control, this kind of samples have been used as superhydrophilic or superhydrophobic surfaces. Such extreme changes in wettability can be achieved by controlling both the surface structuring and its chemical composition.^[436,437]

8. Modelling PC and Disordered Systems

Predicting the optical properties of photonic materials is one of the key issues in photonics. Along with theoretical tools and simplified models, the availability of cheap and powerful computers has allowed the deployment of new numerical techniques fulfilling the requirements of stability, speed and accuracy of simulations of light scattering and emission in complex systems.

In this section we briefly describe some of the numerical techniques used to predict the light transport and emission properties of photonic materials.^[521]

Numerical methods are usually divided in two main categories, namely time and frequency domain methods. Time domain methods consider the spatio-temporal evolution of the electromagnetic fields, while frequency domain methods determine the spatial structure of the fields at a fixed frequency.

Among the time domain methods,^[522] the most powerful and widely used is finite differences time domain (FDTD) method.^[523] The space is discretized in a suitable grid, usually the so called Yee lattice, where electric and magnetic field components are explicitly calculated. Those fields are time evolved according to Maxwell equations in appropriate time steps. This method is relatively easy to implement, there exist several freely available and commercial codes and, essentially, its accuracy is limited only by computational resources and time. It is among the few methods allowing to include nonlinear effects such that it has been used to study nonlinear phenomena in PCs,^[524] and lasing in photonic structures through coupling with Bloch equations,^[525] among others.^[526] Drawbacks of this method include the extensive computational resources needed to accurately solve problems involving a volume of several wavelengths, as the whole simulation volume has to be discretized. Also, the delicate interplay between simulation volume and boundary conditions has to be taken into account to reach physically meaningful solutions.

The vast majority of problems involve linking an external signal to the system's response. If materials present a linear behaviour, the relation between incoming fields and system response is also linear. Depending on the description of stimulus and response different objects linking them are available for the various wavefunction bases that can be considered.

The scattering matrix relates the incoming fields expressed as a superposition of plane waves with the fields scattered by the system in a given direction.

The transition matrix, or T-matrix, is the function relating the incoming and outgoing scattered fields in a given basis, usually vector spherical harmonics.

When the system can be naturally split in two parts, the transfer matrix can provide a useful formulation of scattering problems. The transfer matrix relates the field amplitudes in a given basis at one side of the system, for both incoming and outgoing EM fields, with the amplitudes of fields on the other side.

Then, there exist several widely used frequency domain methods to solve Maxwell equations based on the above introduced matrices and different variants. The scattering matrix,^[527] T-Matrix^[528] and transfer matrix^[529] methods have been successfully used in a variety of large-scale numerical computations. These methods can include both evanescent and propagating waves, hence including near-field effects as those arising in many light emission problems or near field microscopy.^[530]

One advantage of these methods, we find, is its speed and efficiency. Nevertheless, if the simulated system possesses a rich short range spatial structure, the number of basis elements needed to reach a given accuracy may be large. On the other hand, the inclusion of nonlinear effects, although possible,^[531] is far from being trivial and introduces several drawbacks leading to a lower performance of the method.

In the case of perfect PCs, the full solution of the Maxwell equations is suitably found in the frequency domain as the solution of an eigenvalue problem. A widely used method^[532] is based on an iterative solver of Maxwell equations in the frequency domain in a plane wave basis by making use of the Bloch-Floquet theorem. This method, and its associated free software is suitable for obtaining the dispersion relations of the crystal as well as its associated eigenfunctions. When expressing the solution of Maxwell equations as a solution of an eigenvalue problem in the frequency domain, the inclusion of dispersion in the optical properties of the materials constitutes a major difficulty.

Extensive and precise calculations on finite photonic crystals can be performed by means of scattering matrix method with the explicit inclusion of the Bloch-Floquet theorem. This method, widely known as layered KKR method,^[533] has been used in a wide variety of problems involving the calculation of transport properties of finite slabs PC.

When defects are introduced in a PC, several methods in the frequency domain are suited for simulation purposes. Among them, Wannier functions expansions can be used.^[534] This method relies on the construction of an appropriate basis of Wannier functions. The solution to problems with point or linear defects can be efficiently obtained by this method. Even the inclusion of nonlinearities is possible.^[535] A major difficulty of this method is the description of the Wannier basis.

The coupled dipole method or discrete dipole approach (DDA),^[536–538] suitable for small size systems, discretizes the system in a simple cubic lattice; each cell can be considered as a point dipole whose polarizability is given by its dimensions and permittivity. At each frequency a self-consistent set of equations describing the interacting dipoles must be solved. This method allows solving systems with complex geometry, and heterogeneous optical properties. Nevertheless it is limited by the requirement of large wavelength compared to the cell size. It has been generalized to include stratified host media.^[539]

Instead of discretizing the objects and considering each cell as a dipolar particle, it is possible to expand the solution of the

electromagnetic fields in terms of multiple multipoles centred inside each object. Matching the fields at the boundaries lead to a set of linear equations^[540] for each working frequency. Once the system is solved, full information about fields outside and inside the objects is obtained. The main advantage of this method arises when scatterers can support geometric resonances and it can be used to obtain the full Green's tensor of the system.^[541] Nevertheless, as the whole system has to be taken into account, strong limitations regarding the simulation volume and stiffness of the problem arise with this method.

A similar procedure is followed in the point matching method (PMM).^[542] In this method fields are expanded in a suitable basis, usually vector spherical harmonics centred at scatterers whose boundaries are discretized. In its generalized form, matching conditions of the electromagnetic fields at the boundaries of scatterers are imposed at an oversampled set of points, resulting hence in an overdetermined set of equations for the field amplitudes which is solved by least squares fitting. This method is by nature very stable once the sampling points and basis for the fields are properly chosen. A drawback is the difficult choice of a suitable basis to expand fields.

DDA, PMM and multipolar expansions can be considered as different formulations of the problem in terms of the T-matrix. A different approach leads to the method of moments (MoM) when the field equations are considered in a slightly different way.^[543] If the electromagnetic response of the object under consideration is homogeneous, the whole electromagnetic scattering problem can be recast in the form of surface integral equations, leading hence to boundary element method (BEM).^[544] In this method only electric and magnetic fields at the boundaries enclosing homogeneous objects has to be considered. Hence, if the surface to volume ratio is small, this method can take great advantage over naturally volume-based methods. Being one of the oldest numerical methods in electromagnetism,^[545] several new approaches using fast Fourier transform techniques provide better performance and high order accuracy^[546] to this method.

Selecting a computational tool critically depends on the details of the particular problem to be solved. There is no general purpose method suitable for any kind of problem while keeping speed and accuracy. A number of software packages are available, either proprietary or free software. Several researches in the field of computational electromagnetism have compiled listings of available software. We refer the reader to the web site built by T. Wriedt *et al.*,^[547] where a compilation of available electromagnetic codes is provided. A. Moroz,^[548] compiled a set of links to different codes and other digital resources that can be found in the web.

Despite the large number of freely available codes it is worth mentioning a few of them which have been proved to be reliable in a wide range of problems.

MEEP is an open source FDTD code based on ref.,^[549] that can be found at their MIT site.^[550] It provides a general purpose method to solve relatively complex electromagnetic emission and transport problems in the time domain. A complementary code, provided by the same research group, is known as MPB.^[551] This code, freely available, calculates the band structure, including the electromagnetic eigen-fields of a perfect PC in 2D or 3D.

A code based on the above mentioned DDA method has been developed by B. T. Draine and P. J. Flatau. This code is known as DDSCAT and can be found in their web site.^[552] It is a very stable, fast and accurate set of numerical routines suitable to perform calculations of light emission and transport in relatively small systems but possessing an arbitrary complex geometry and non-homogeneous optical response.

A code based on the T-matrix method, developed by M. I. Mishchenko, L. D. Travis, and D. W. Mackowski can be found in their page.^[553] This code is suitable for problems involving light scattering by a large set of spheroidal particles, allowing calculating statistical transport properties of collections of particles placed and oriented at random.

Of course the above paragraphs do not pretend to be exhaustive, we provide an incomplete listing of just a few methods and software packages. We refer the reader to the above mentioned internet sites, or to the major web search engines, for a more comprehensive list of available tools.

9. Summary and Outlook

After more than fifteen years self-assembled PCs have matured and grown to a full-fledged materials discipline and have even gemmated a new field where the concept of glass as opposed to crystal has acquired full meaning in photonics. Apart from serving as a fertile playground where most photonic concepts can be tested and new ones explored, self-assembled PCs and glasses have realized many applications and hold promise for more. However the most differentiating feature of this sort of materials is their inexpensiveness and their potential as cheap raw matter where actual devices can be fabricated. Even if these were never forthcoming it is undeniable that many advances have been achieved in other disciplines in the route to perfecting synthesis of fine particles, self-assembly, and processing this type of materials. While progress in the field has fed from eminent scientists in various disciplines, chiefly physics and chemistry, the labour has been fragmentary perhaps because a strong associated industry behind it is lacking. This is at variance with a competing technology, dominant nowadays in the field, such as is microlithography-based photonics. In this sense it can be said that self-assembled photonic structures dearly suffer from amateurism. However with the unavoidable growth solar photovoltaics, among the sustainable energy sources, must experience; and the momentum catalysis and purification will be gathering in the near future, the need for photonic materials other than those in the form of integrated circuits will become pressing. Much the same can be said about efficient disposable light sources where self-assembled systems may find a niche. It is expected that the growing field of bio-inspired materials will provide a source of inspiration and merge with or even take over self-assembly techniques. Rapid progress is being made and heed should be taken where nature's routes may lead. The best of the tale is that its end has not been told yet and a bright future may still be expected. At any rate a lot of science may still lie ahead if only in the area of complexity both regarding the structure and the photonic response.

ACKNOWLEDGEMENTS

This work as supported by MICINN project MAT2009-07841, Consolider CSD2007-0046 and CSIC PIF08-016; M.I. and R.S. acknowledge the MICINN Ramón y Cajal programme, J.F.G. acknowledges the CSIC JAE programme, L.S.F. acknowledges the MICINN Juan de la Cierva programme.

Received: January 29, 2010

Revised: April 16, 2010

Published online: September 27, 2010

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