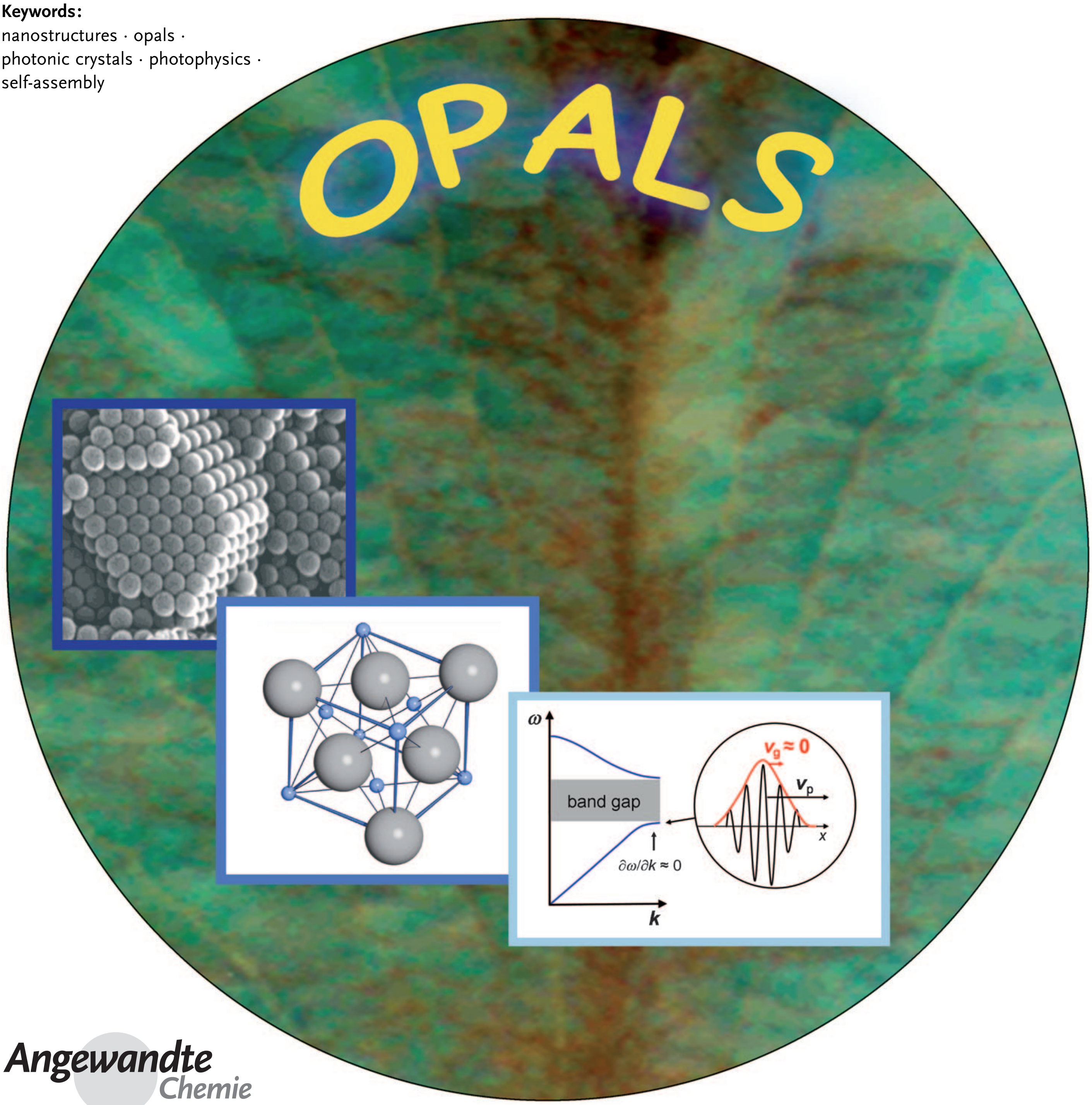
DOI: 10.1002/anie.200900210

Opals

Opals: Status and Prospects

Frank Marlow, Muldarisnur, Parvin Sharifi, Rainer Brinkmann, and Cecilia Mendive*

Keywords:
nanostructures · opals · photonic crystals · photophysics · self-assembly



The beauty of opals results from a densely packed, highly ordered arrangement of silica spheres with a diameter of several hundred nanometers. Such ordered nanostructures are typical examples of materials called photonic crystals, which can be formed by known microstructuring methods and by self-assembly. Opals represent a self-assembly approach to these structured media; such an approach can lead to novel materials for photonics, photocatalysis, and other areas. Although self-assembly leads to many types of defects, resulting in the surprising and very individual appearance of natural opals, it causes also difficulties in technological applications of opal systems.

From the Contents

1. Introduction

Opals have been known since ancient times. They are an unusual type of gemstone: They are not hard, they do not impress with their regular geometrical shape, but they amaze observers with their coloration, which changes when the stone is moved. This mysterious property is called opalescence (see Section 7.1). It was recognized long ago that this property also occurs in many other natural and artificial structures. It is now generally known that this coloration results from a periodic nanostructure (Figure 1). Biologists call such opalescent systems "structural colors", and they appear quite frequently in the biological world; physicists name them "photonic crystals". These systems have a periodicity on a scale that is comparable with the wavelength of visible light. As a result, they exhibit many of the special crystal properties for photon propagation that are normally known for electrons, such as the occurrence of bands and band gaps.[1] Opals are a useful prototype for such systems.

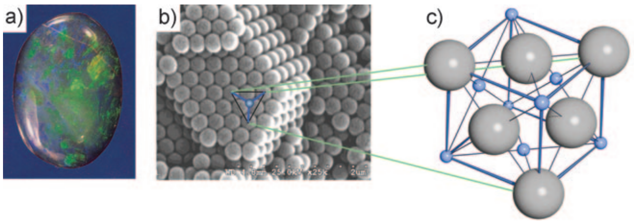


Figure 1. a) A natural opal (for details, see Section 2.2); b) SEM image of the opal nanostructure, which is responsible for the color effects by interference; c) the fcc lattice used for the description of the nanostructure lattice.

The role of opals as a prototype for photonic crystals is twofold. Firstly, opals are three-dimensional periodic systems, which are the most interesting photonic crystals from the point of view of dimensionality.[1] Secondly, they represent a basic fabrication approach employing self-assembly mechanisms (bottom-up techniques) for photonic crystals. Photonic crystals in general can be fabricated by both bottom-up and top-down approaches. These approaches compete with each other, but combinations of both are possible.

The theory of light propagation in opals and inverse opals (see Section 6) is well-developed. Opals never have a so-called complete photonic band gap, which is a central property of photonic crystals.[1] Inverse opals can, however, exhibit this important property.[2] The required parameter ranges and realistic tuning possibilities have been theoretically studied in detail.[3] These studies have led to many experimental attempts to realize such a band gap (see Section 6 and 7), which is important for applications and from a fundamental point of view. With a complete band gap, opal-related systems can have all the basic photonic crystal properties.

The prototypical role of opals seems to us a good reason to have a closer look at the research field. Interesting reviews (for example, references [4–7]) with a different focus have already appeared; nevertheless, the field is developing continuously. It is the aim of this review to show the current status and to deal with the question how the opals fulfill their prototypical role. Are there already useful materials available? Is the self-assembly approach still promising in the field of photonic crystals?

Opals are also key examples for some related research fields, such as structural colors,[8] colloidal lithography,[9] and colloidal crystals.[10] These fields have many common aspects, but they have different aims. Structural colors are natural or artificial systems with colors produced by interference effects of a nanostructure. Colloidal lithography uses two-dimensional ordered arrangements of microspheres as masks for structuring processes. Colloidal crystals are a more general class of materials than opals. They can be formed from colloidal suspensions in several ways owing to different particle–particle interactions and a variety of possible changes of the external parameters of a suspension. Opals

---

[*] Dr. F. Marlow, Muldarisnur, P. Sharifi, R. Brinkmann, Dr. C. Mendive
Max-Planck-Institut für Kohlenforschung
45470 Mülheim an der Ruhr (Germany)
E-mail: marlow@mpi-muelheim.mpg.de
Homepage: http://www.mpi-muelheim.mpg.de/marlow.html

are only a special case of these ordered periodic arrangements. These specific colloidal crystals are simple to fabricate and they can be used for extended macroscopic three-dimensional systems. It is very likely that this specification results in the restriction of the many possible particle–particle interactions to effective repulsive forces. Other aspects of colloidal crystals, such as the restriction to two dimensions, non-spherical building blocks, dislocation dynamics, and phase[11] and glass transitions[12] in colloidal systems, are highly interesting but have a wider aim than efficient fabrication approaches for opals. They can provide much new knowledge on structure formation and they can lead to new structures. However, the colloidal systems thus used have mostly lost the decisive potential advantage of the ordinary opal systems: to be a source for three-dimensional photonic crystals that can be fabricated fast, cheap, and with good quality.

Many theoretical approaches in colloid crystal science are general, which is also the reason for their limited applicability for opals. They aim to understand colloidal systems involving many different interaction possibilities between the particles. Good opals however are fabricated by a few deposition methods, normally using charge-stabilized suspensions. They apply technically simple recipes that are however relatively complicated from a theoretical point of view.

We shall begin by looking at opals from a phenomenological point of view by regarding opal shapes (Section 2) and deposition methods (Section 3); then we will analyze their mechanism of formation and structure (Sections 4 and 5), and finally we will consider their uses (Section 6 and 7).

2. Opal Shapes

Naturally occurring opals differ in appearance, being either macroscopic pieces, or inclusions in matrix stones, or thin coatings. Artificial opals are also fabricated in various forms. The mechanisms of synthesis and the properties and

Frank Marlow studied physics at the Humboldt University in Berlin and completed his doctorate in 1988 under Werner Ebeling. He then went to the Institute of Physical Chemistry of the former Academy of Sciences in East Berlin, was a postdoc at the Free University Berlin, and joined the Institute of Applied Chemistry in Berlin-Adlershof. Since 1999, he has been at the Max Planck Institute for Coal Research, where he currently leads the research group "Nanostructures and Optical Materials". Among his previous awards is the Leopoldina Förderpreis. He is one of the founders of the International Max Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS SurMat).

Rainer Brinkmann finished his studies on chemical engineering at the FH Aachen in 1973. Since then he has worked at the MPI for Coal Research in Mülheim an der Ruhr on colloidal systems and nanomaterials.

Muldarisnur was born in 1981 and graduated with a BSc in physics from Padang State University (Indonesia) and an MSc in physics in 2006 from Bandung Institute of Technology (Indonesia). He was awarded a scholarship from the International Max Planck Research School SurMat to carry out doctoral research working on growth processes of opaline photonic crystals in the group of Frank Marlow at the Max Planck Institute for Coal Research.

Cecilia Mendive was born in 1973 in Buenos Aires (Argentina). She studied chemistry at the University of Buenos Aires, and received her PhD in 2007 from National University of San Martin (Argentina) after working in Argentina and Germany with Miguel Blesa (Argentina) and Detlef Bahnemann and Thomas Bredow (Leibniz University of Hannover, Germany). After postdoctoral research with Detlef Bahnemann, she joined the Max Planck Institute for Coal Research in 2008 to work on self-assembled photonic crystals films.

Parvin Sharifi was born in 1976 in Tehran (Iran). She received her BSc in applied physics from Ferdowsi University of Mashhad (Iran) and subsequently her MSc in physics in 2003 from K.N.T. University in Tehran. She was awarded a scholarship from the International Max Planck Research School SurMat to undertake doctoral research on slow photon effects in photonic crystals in the group of Frank Marlow at the Max Planck Institute for Coal Research.

potential application fields of the various forms are different. The distinction between opal shapes is therefore useful and serves as a first method of opal classification.

2.1. Porous Opal Layers

For applications as photonic crystals, opal layers can play an outstanding role. They can be a platform for the fabrication of waveguide-based devices, and they are compatible with many known structuring technologies. As long as the layers are porous, they are amenable to a variety of modifications, and in particular inversion processes. As a result of these considerations, opal layers are given special attention in this review. Depending on the fabrication technique, the layers have a thickness ranging from several monolayers to several hundred micrometers.

At the micrometer scale ($< 1\ \mu m$), the opal layers exhibit nearly perfect fcc lattices, as do all opals, with the feature that the (111) direction is aligned perpendicular to the film (Figure 2). On a larger length scale (about 100 μm), very prominent types of defects, namely cracks, appear in all opal layers. Their arrangement depends characteristically on the fabrication technique used; for example, disordered networks or parallel lines are known. Macroscopically (> 1 mm) the films show a single, but milky opalescence color, which is a consequence of the alignment of the (111) direction. Cracks and slight color fluctuations are only visible to an experienced observer.

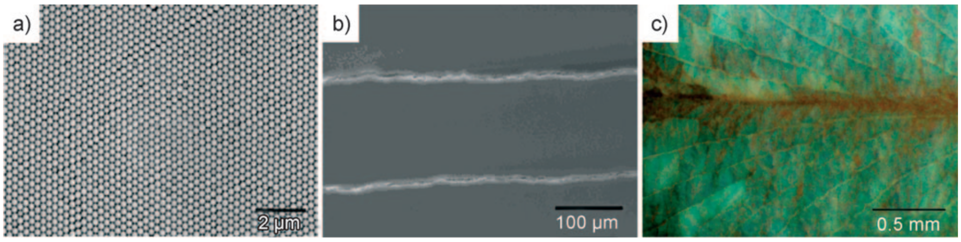


Figure 2. a) SEM image of an opal film in the normal direction; b) lower magnification SEM image, showing cracks in the film; c) optical microscopy image.[13]

2.2. Natural Opals

Natural opals are found all over the world and are considered to be valuable gemstones. They show all colors, though very often they are slightly milky with a greenish-bluish play of colors. Their density lies between 2.0 and 2.2 g cm^{-3}, and their hardness (Mohs scale) is between $5^1/_2$ and $6^1/_2$.[14] They contain varying amounts of water (mostly 4–9 %, sometimes 20 %),[14] and consist of silica in which impurities such as Fe^{3+}, Al^{3+}, or Ti^{3+} can be found.[15,16] Silica spheres with diameters ranging from 150 to 400 nm are often amorphous, but frequently they can also contain crystobalite and tridymite,[16] forming imperfect stacking layers.[14] One differentiates between two groups, so-called precious opals (or noble opals) with a visible play of colors, and common opals (also called potch) without the color play.

The word “opal” is used in this review for a whole class of materials, but in its original sense, the term refers to natural opals. The word comes from Sanskrit (*upala* means “precious stone”), than it was used in Latin and Greek, *opalus* and *opallios*, both meaning “to see a color change”. Famous opal lovers were Mark Anthony, who is said to have assaulted a senator for refusing his offer of a large amount of money for an attractive opal, and Napoleon, who used opals in his crown and presented his empress Josephine the famous “Burning of Troy”. Shakespeare called them “*the miracle […] and queen of gems*”.[17,18]

Precious opals are considered to be one of the most beautiful gems owing to its play of color. In former times, the coloration of opals was believed to arise from contaminants, internal cracks, or liquids trapped within.[17] The first almost correct explanation was proposed by Raman and Jayaraman,[19] who suggested that the colors arise from diffraction of light by regular arrays of silica layers with differing refractive index. Finally, it was shown by Sanders et al.[20–23] in the mid-1960s that the diffraction at regular arrays of silica spheres is responsible for the colors. Electron microscopy showed that opals consist of periodic three-dimensionally arranged silica spheres of submicrometer size.

The mysterious character of the opals is inherently connected with their very individual patterns, which are arrangements of different color domains that are each dependent on viewing angle. This individual pattern has led to many examples of opals having special names; for example, Eckert[17] gives a description of about 100 named opals. These very valuable singular gemstones can have domains of several millimeters in size. In very seldom cases, the domains can form a more or less regular pattern, such as in opals known as harlequin. Impressive pictures can be found in many publications (for example in reference [24]) or books (especially in reference [17], see also Figure 1 and Figure 3).

Less-expensive examples of precious opals have millimeter-sized single-color domains with very individual irregular shapes. The color of the domains is not fully homogeneous, but appears to fluctuate slightly in the sub-millimeter range. Inexperienced observers are not truly able to distinguish between color and local brightness in these fluctuations. Similar fluctuations are also visible in all the photographs published in textbooks.

In nearly all opals, the pores between the silica spheres are filled with water-containing silica. This filling gives the opals mechanical stability and lowers the refractive index contrast, which is advantageous for the visual impression, as it reduces scattering. As a result, the opal appears less milky and the colors seem to come from deeper regions. There is only one special sort of natural opals known that have very incomplete

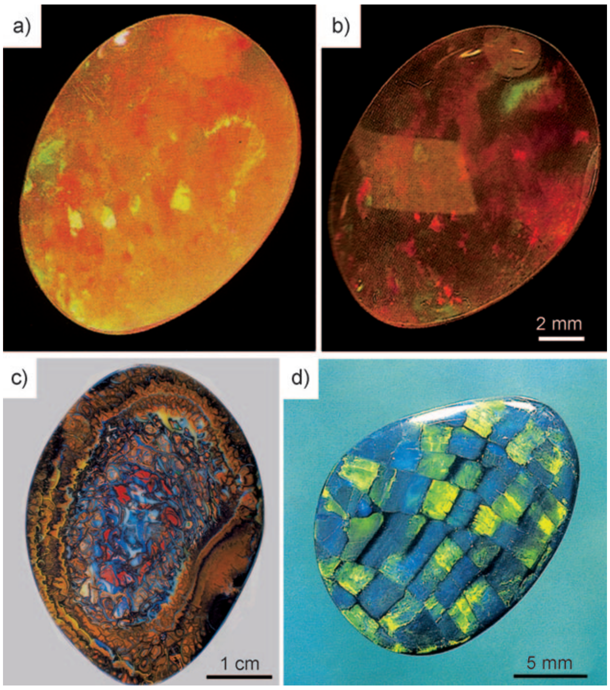


Figure 3. Natural opals. a) A hydrophane opal with a milky appearance and one of the typical colorations of opals; b) The same stone as in (a) but in the hydrated state. It shows another typical coloration of opals; c) An iron oxide-containing matrix opal; d) A harlequin. (Pictures from Ref. [17] and [24]; scale bars estimated from Figure captions).

filling, the so-called hydrophane opals.[17] Their optical properties change dramatically from milky to transparent when water soaks into the open pores.

Another interesting aspect of natural opals is their occurrence together with various other stones and minerals. They are found in both volcanic and in sedimentary environments. There are many indications that they are formed by relatively young leaching and deposition processes, such the existence of a special class of opals called boulder or matrix opals. Figure 3c shows such an example in which the opal seems to fill another stone.

The origin of “church window” opals having a mosaic pattern (see Figure 4) is not fully understood. It seems that these opals are formed by cracking of an older original opal in pieces and then refilling the cracks with new suspension. Opalescent color effects can be seen in the pieces and in the filling between them. Other remarkable types of opal are opalized fossils originating from wood, bones, shells, and snails, which consist of partially of opal material or have a thin opal coating. These many examples illustrate the variety of opal shapes and point to a variety of different formation conditions and formation times.

2.3. Compact Artificial Opaline Systems

Fabrication of artificial opals with the aim of imitating natural opals dates as far back as 1972, when the company Gilson (Ets. Ceramiques Pierre Gilson, France) presented its first examples. These artificial opals have a typical growth structure and can be easily differentiated from natural opals.[17,18] This also applies for Japanese (Inamori opals) and Greek opal imitations. Although it is known they are prepared by sedimentation,[18] the detailed fabrication techniques have been kept largely confidential by the manufacturers. The first scientific publication reporting opal imitations appeared in 1989.[25]

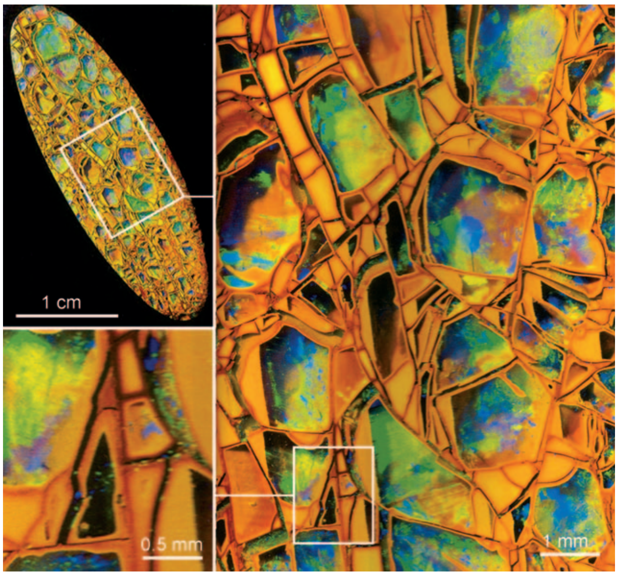


Figure 4. A church-window opal at different magnifications (Pictures from Ref. [24]; scale bars estimated from Figure captions).

Imitating opals as such is no longer an especially crucial aim; instead, interest has turned to the development of opal fabrication techniques for photonic purposes. Moreover, in the current techniques, efforts are invested in avoiding the characteristic feature that makes natural opals charming and individual, that is, the unique colorful pattern that in scientific terms is only a statistical domain structure. Nevertheless, the older opal imitation methods provide interesting knowledge about reproducibility and controllability of some opal fabrications.

One of the important non-optical properties of an imitation opal is its hardness. As simple sphere assemblies are fragile, hardness is achieved by filling the interstitial space with water-containing silica, yielding compact systems which can be easily manufactured for jewelry, for example, by cutting and polishing. From the point of view of applications, the silica infiltration not only improves the stability but also reduces the porosity and consequently the potential of the opaline system to undergo modification.

Interesting examples of compact opaline structures were introduced by Hellmann et al.[26,29] These preparations consist of a melt-compression (extrusion-like) technique using core–shell latex particles with a rigid thermoplastic core and a soft grafted elastomeric shell. This rubbery polymer is not confined in a cavity but allowed to flow freely sideways whilst being pressed by two plates at 150–170 °C and 150 bar. Normally, the final product is a 0.1–0.3 mm thick film. In samples obtained from these hard core–soft shell spheres, the hard cores form an fcc lattice with the soft shells in a matrix around them. The spheres are well-ordered near the surface with a large increase of disorder towards the center of the films. The local order thus achieved is not simply a consequence of a volume reduction by compression, but more likely a result of the shear stress, which is largest near the surfaces. Like extrusion, the process is irreversible and can be described by a quasi steady-state flow with a strong velocity gradient. This can lead to dissipatively ordered states that result from minimizing the entropy production.[27] One explanation of such a dissipative ordering mechanism may be that the viscosity of the ordered state is larger than in the disordered state. Because entropy production is related inversely to viscosity here, the behavior of the viscosity could explain the dissipative ordering mechanism. More investigations are, however, required to fully clarify the nature of the underlying ordering processes.

The melt-compression method is fast and provides large crack-free films (see Figure 5) that exhibit beautiful colorations. Such techniques are easily compatible with current polymer processing techniques. The elimination of cracks is clearly a structural improvement when compared to alternative kinds of opal film formation; however, all other types of defects remain present. Furthermore, the flexibility of these systems allows defects combined with continuous lattice distortions. Slightly smaller, larger, or missing spheres introduce distortions yielding bent rows, as depicted in Figure 5c. Furthermore, the pressure applied during the opal preparation may deform the spherical nature of the lattice units (Figure 5d). The deformation is useful for the fine tuning of the optical properties[28] if it can be controlled in a desired manner.

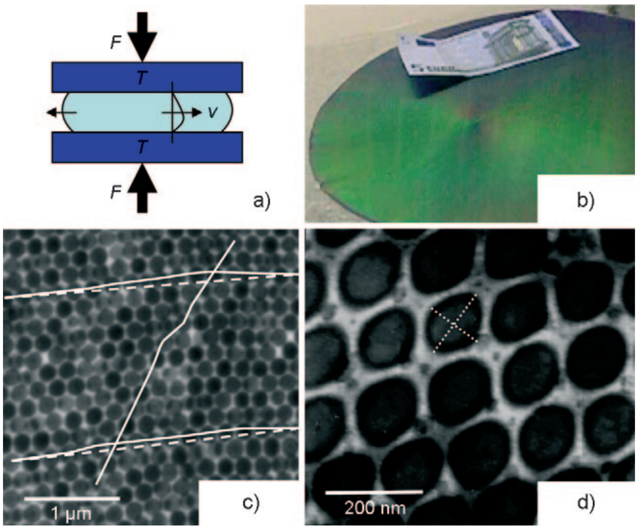


Figure 5. Compact opaline structures fabricated by an extrusion-like process.[29] a) The application of force (*F*) and temperature (*T*) results in a flow profile (*v*); b) Large colorful opal film with a €5 banknote to indicate the size of the film; c) An ordered sphere arrangement showing deviations from a perfect lattice. Three examples are marked with solid lines; two sphere rows have been marked with dashed straight lines to better show the deviations; d) Distorted spheres. The ratio of the two marked perpendicular axes is about 0.8:1.

The films are attractive materials that have reflection colors that are dependent on the observation angle. However, the refractive index contrast of these purely polymeric films is too small to produce stronger photonic effects (for example, large band gaps). Furthermore, the statistical lattice distortions make their photonic behavior difficult to predict. Therefore, the multiple color effects of these materials can find application for decoration purposes, but they encounter serious limitations for their use in photonic devices. Three properties of these materials, namely their inherent low refractive index contrast, the lattice distortions, and their low porosity, have hampered further improvements in engineering their optical properties. In recent work however, the transformation of some of the compact layers into porous inverse opal layers by etching was reported, thus possibly overcoming two of the drawbacks.

2.4. Opaline Supraparticles, Random Pieces, and Microstructures

The geometric restriction of the opaline arrangement is an important technological issue, as only relatively small opal lattices are needed for potential photonic devices. It can be envisaged that very small opal particles in composite materials can be used for decorative applications as well. Therefore, for some applications it is useful to confine the opaline material to small regions during the fabrication process.

Very beautiful opaline samples were recently produced by Velev et al.[30] They dried droplets of suspension on surfaces, which resulted in small particles. These supraparticles can be fabricated very easily and relatively quickly, but as a result of the curved surface, they necessarily contain many defects. These defects are highly visible in similar samples produced by Merck,[31] which tested spray drying to accelerate the growth still further. It is possible that this fabrication method additionally increases the defect concentration. Despite these drawbacks, both techniques could be interesting strategies for mass fabrication (Figure 6).

Opal fragments are also often the result of sedimentation, evaporation, or filtering[34] processes with larger amounts of suspension. The solid that forms falls apart in many rather undefined pieces resulting from cracks formed during drying. Locally, the cracks are compatible with the opal lattice, but on a larger scale they are randomly shaped. It is difficult to use

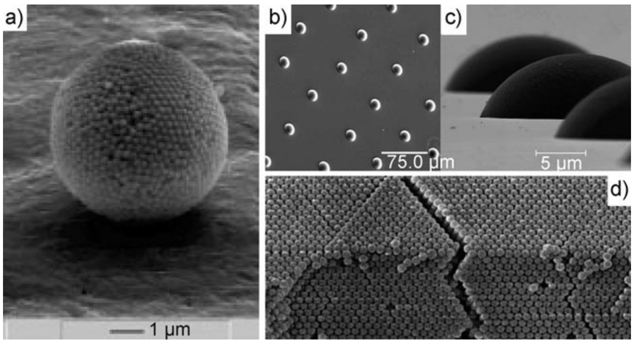


Figure 6. Supraparticles formed by a) spray drying[31] and b,c) ink-jet printing;[32] d) Cracks that lead to opal fragments.[33]

such pieces in applications, but they can be useful in experiments; for example, for the inversion of opals (see Section 6).

An interesting option in this direction is the arrangement of the individual photonic particles into arrays (see Figure 6b,c).[32,35] The fabrication is made possible with inkjet printing, which is currently extensively used for material deposition and structuring. Such arrays open up possibilities for applications either after the problems with the defects in the individual particles are solved, or for photonic applications that are insensitive to disorder.

The incorporation of small opaline arrangements in patterns formed by microstructures has also attracted some attention (Figure 7).[36,37] These microstructures can be envisaged as being an element of a future microoptic device. At first glance, the fabricated structures look like parts of integrated photonic circuits. Looking more closely, however, these structures bring about new inherent problems connected with the fitting of the opal lattice to the supporting template: Every misfit and every inaccuracy of the template is transferred to the opal. The self-assembly of the opal lattice is strongly guided and, therefore, less perfect than in a larger volume. It is an interesting fundamental question how and how far surfaces influence the volume structure.

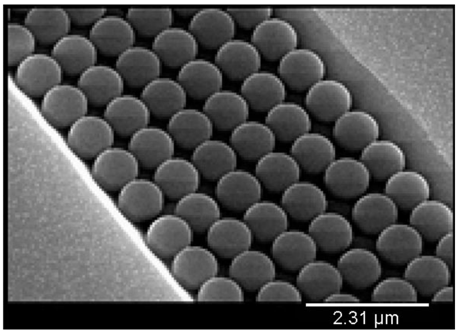


Figure 7. An opaline arrangement in a V-shaped groove in silicon.[36]

2.5. One- and Two-Dimensional Colloidal Crystals

Systems with a lower dimension that are made up of ordered microspheres are also often considered to be opals. One-dimensional colloidal crystals[38] are chains of spheres or more complicated rope-like arrangements[39] that also show interesting optical effects. Monolayers of spherical nanoparticles can be easily prepared[40] and represent two-dimentional photonic crystals that also have typical photonic effects. A large number of publications[41] deal with the use of these two-dimensional colloidal crystals as masks for etching and deposition. They have very interesting applications for surface patterning in the nanometer range. These two-dimensional systems are similar to opals, but because of their reduced dimensionality, they are not opals in a strict sense. The field is often called colloidal lithography or nanosphere lithography; these two names could cause confusion, as the technique is not really an extension of traditional lithography methods as these names would suggest. Lithography means the ability to write widely variable, arbitrarily extendable, and arbitrarily complex structures (pictures, books, devices). In contrast, colloidal lithography allows the writing of periodic or disordered patterns only. All information, complexity or functionality must be contained in one pixel.

It is worth noting that the mechanism leading to the formation of one- or two-dimensional colloidal crystals is different from opals. In the lower dimensional system, a meniscus is formed towards the missing dimension, which induces strong capillary forces between the spheres that have a decisive influence on structure formation. In going from a monolayer to multilayers, the capillary forces are increasingly unimportant because the inner part of a thicker layer stack is totally wet during crystal formation, which excludes the effect of the meniscus and consequently also the influence of capillary forces.

3. Deposition Methods

3.1. Overview

All opal fabrication methods start with a suspension of monodisperse particles that have to be regularly arranged. Various methods are known that achieve this aim; among these are sedimentation, either by gravitation[42–44] or electric fields,[45–47] evaporation assembly onto horizontal[48,49] or vertical[50] substrates, and deposition in physical confinement cells.[13,51] The methods are simple and deliver good films or opal pieces; however, knowledge about the underlying ordering process is still not complete. In this Review, the deposition methods are classified according to the dominant driving force during the ordering. Of course, this classification is a matter of interpretation; nevertheless, we shall consider three main classes of opal deposition: field-induced deposition, volume restriction, and flow-induced deposition (Figure 8).

The lack of any methods delivering two-dimensional opaline assemblies in this classification might be surprising. The absence is due the fact that this review is restricted to three-dimensional systems, which was done for two reasons. The first is their wider potential applications, and the second is that the ordering in two dimensions can involve a larger number of efficient mechanisms than in three. Two-dimensional ordering can also occur during drying whereas only wet-phase ordering seems to be possible in three-dimensional systems.

It might also be surprising that only methods using stable suspensions appear in Figure 8. It appears that the fabrication of all practical opal systems is based on repulsive interactions between spheres in suspension and an external action (field, flow, volume change) driving the particles together and thus overcoming an repulsion barrier. The suspensions that were successfully used consist of charge-stabilized particles, and thus repulsive forces dominate between the particles. The destabilization of such suspensions would lead to dominating attractive interparticle (van der Waals) interactions. The ordering effect of such a treatment seems obvious and straightforward; however, no example is known in which

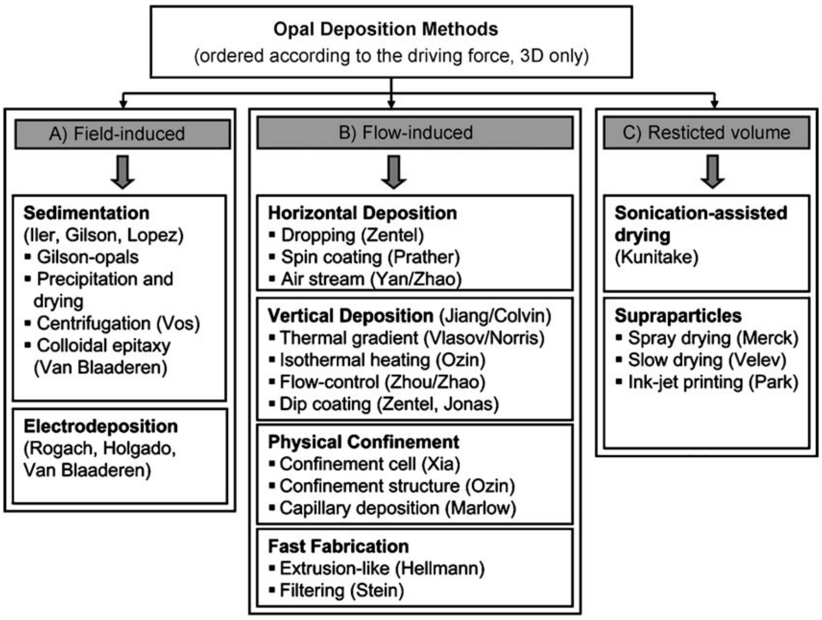


Figure 8. Classification of opal deposition methods. The list is restricted to methods producing macroscopic three-dimensional opaline arrangements. In the order of occurrence, the author or group names refer to publications on sedimentation,[42,52,44,53,60] electrodeposition,[45–47] horizontal deposition,[48,66,49] vertical deposition,[50,120,71,76,37,54] confinement,[51,36,13] fast fabrication,[26,34] sonication assistance,[55] and supraparticles.[56,30,32]

the ordered regions formed in such systems have been transferred into a solid macroscopic material that can be described as an opal.

Two of the three classes (A and C) only contain methods that most likely belong to the classical conservative[27] structure formation. In these cases, the concentration of particles increases until it exceeds a critical concentration, leading to a thermodynamically favored crystal formation. In class C, this is done by lowering the suspension volume, whereas in class A, a field drives the particles together. Non-equilibrium effects are only expected to lead to disturbances of the structure, such as growth defects and disordered domains.

In flow-induced deposition methods, not only conservative structure formation but also non-equilibrium processes (dissipative ordering mechanisms)[27] can play a role. In the conservative processes, the flow is only used to achieve a high-concentration region that exceeds the concentration required for colloidal crystallization. In non-equilibrium processes, the flow directly leads to the assembly controlled by a minimum in entropy production. From a microscopic point of view, spheres are often driven by the flow of suspension towards a growth front, and they stick together through a stochastic process at this front. The basic thermodynamic mechanism, however, needs to be investigated for every specific example in detail.

Monodisperse colloidal particles are the basis of all these opal depositions, and are now commercially available from many companies. Silica, polystyrene, and poly(methyl methacrylate) (PMMA) suspensions are the most commonly used starting materials. Before 1965, monodisperse silica suspensions were occasionally observed (as summarized by Iler[42]). Later, the work of Stöber et al.[57] provided an easy and now-established procedure to fabricate such particles. For polymer particles, surfactant-free emulsion polymerization is a very popular method for the preparation of monodisperse spheres.[6]

Non-spherical building blocks for opal-like structures should offer a number of new possibilities for optical effects. Microfabrication and opal distortion have been discussed for this purpose. Recent pioneering work has been carried out by Stein et al.,[58,59] who used disassembly techniques on other structures, such as inverse opals, to fabricate new building blocks. Uniformly shaped nanoparticles (mainly cuboids and tetrapods) have been synthesized. The key idea is that continuous structures can be cleaved at weak connection points either chemically or by mechanical forces. Arrays of such particles should preferentially form non-fcc structures. In special cases, non-fcc arrangements such as simple cubic lattices have already been observed.

3.2. Field-Induced Deposition Methods

Sedimentation driven by gravitational force is the conceptually most straightforward method for opal deposition. In this method, colloidal particles are allowed to settle onto a flat[42,43] or patterned[60] surface. The interplay between gravity, electrostatic repulsion, and Brownian motion appears to be crucial for the formation of the colloidal crystal sediment. The structure obtained is dominantly face-centered cubic, with small fraction of hexagonal close-packed or random close-packed regions. This dominance was attributed to a slight entropy difference between these arrangements in calculations by Woodcock.[61]

The sedimentation method is slow and only applicable for a limited range of sphere sizes because of low sedimentation rates for small spheres and bad ordering for large spheres. It results in samples consisting of differently oriented domains owing to simultaneous nucleation in different locations and subsequent crystal growth.[62] These domains form a typical column-like structure in natural opal imitations (Section 2.3), resulting in a so-called lizard-skin surface effect.

Centrifugation, higher temperatures, and external electrical fields have been proposed for faster deposition. Some treatments have also been proposed to improve the ordering of sediment opals, such as deposition under oscillatory shear[63] and sonic fields.[64]

3.3. Flow-Induced Deposition Methods

In handling monodisperse suspensions, opalescent coatings and droplets are often observed. Therefore, one of the simplest and very effective fabrication approaches is to dry a thin suspension film made by dropping small amounts of suspension onto horizontal hydrophilic supports.[48,49] A characteristic of this method is the strong film thickness fluctuation, with the thinnest part in the middle of the film. This effect is explained by the film growing from the outside, where the opal is formed first, towards the inner part of the film, which dries last. As a result, this method is an example of flow-induced deposition. Understanding the mechanism enabled the improvement of the method by using air streams that induce a growth direction.[49]

A modification of horizontal deposition by employing spin coating has been proposed by several authors.[65,66] The success of this method strongly depends on carefully choosing spinning speed, suspension viscosity, and solvent evaporation.

The recently most widely used opal deposition method was introduced by Jiang et al.[50] and consists of immersing a substrate into a suspension vertically instead of horizontally. The authors coined the phrase "vertical deposition" for this method (Figure 9). It uses the flow of suspension to the substrate induced by the evaporation of solvent in the already-deposited opal layer. This method turns out to have several advantages over sedimentation, such as a smaller amount of suspension needed, lower defect concentrations, easier sample handling (as it is grown on a solid substrate), and good definition of the opal layer surface.

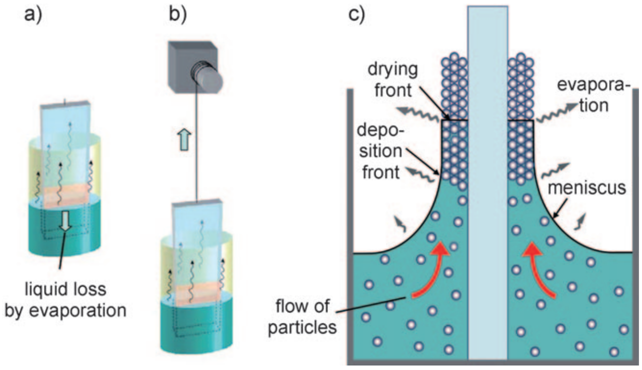


Figure 9. Vertical deposition: a) Original setup; b) combination with slow lifting of the sample; c) assumed processes. (Picture parts are adapted from Ref. [6])

The initial vertical deposition method was limited to small spheres only, which do not sediment quickly. Vertical deposition is relatively slow as it relies on natural evaporation, and shows thickness gradients because the suspension concentration increases as the solvent evaporates.[67] The growth can be efficiently influenced by many parameters, such as initial sphere volume fraction, temperature, relative humidity, substrate tilting angle, and the substrate material.[68,69] For larger spheres, this method has been improved by applying a vertical temperature gradient in the suspension container,[70] by isothermal heating,[71] and by mechanical agitation.[72] The evaporation rate can be increased by the use of ethanol as a solvent instead of water, applying low pressure,[73,74] and heating the suspension. Attempts have been made to avoid the thickness gradient by lifting substrate out of suspension[37,75] or lowering the surface of suspension with a peristaltic pump.[76]

Another approach in this group of methods uses confinement cells, which inherently leads to smooth surfaces and easily controllable thickness. Xia et al. introduced a method of opal deposition into the space between two parallel substrates separated by thin microstructured spacer acting as a filter.[51] External pressure was used as the driving force to transport the spheres. Nevertheless, they reach the already deposited opal in a similar way as in the vertical deposition method. The spheres are then assembled under the strong influence of the flow. Using this method, well-ordered films having a controlled thickness and of several square centimeters in size have been successfully created. A small difficulty arises in the building of the confinement cell and the fabrication of the microstructured filter. This confinement method has also been combined with substrate surface patterning to control the lattice structure and orientation of crystals.[77]

A method that avoids the membrane and the pressure used in that of Xia et al. was developed by Li et al.[13] They used an open cell; the suspension enters the cell by capillary forces and is kept flowing by evaporation. The technique is called the capillary deposition method (CDM), as it is essential that the confinement cell acts as a capillary. The opal assembly process takes place at a moving front in the cell however, and is driven by the flow of the suspension towards the already grown opal that is penetrable to the suspension solvent. Details will be given in Section 3.5.

3.4. Deposition by Volume Restriction

The two most popular methods of opal deposition (sedimentation and vertical deposition) are relatively slow. It is believed that this has a positive effect on the quality of the opals, although there is no real evidence to support this assumption. Therefore, it is important to note that a much faster deposition method used by Kunitake et al.[55] can possibly deliver opals of a similar quality as sedimentation. This method could be called sonication-assisted homogeneous drying, and consists of drying a homogeneous suspension film. The suspension is kept homogeneous as long as possible by the application of ultrasound.

This method seems to be a simple variation of the horizontal deposition methods, but we believe that it has a significantly different deposition mechanism. The ultrasonic conditions avoid the formation of a lateral deposition front and the film is kept homogeneous in the lateral direction. The evaporation necessarily leads to a gradient, but it is perpendicular to the film. Consequently, the opal formation front will also move perpendicular to the film; that is, only over a very short distance which means that the film can be potentially formed much faster. In contrast to the other horizontal deposition methods, liquid flow also seems to be less important over this short distance. For this reason, we have assigned this method to another mechanistic class. It is worth noting that the method is simple and enables large-area layers.

For the supraparticles described in Section 2.4, volume restriction could also be the dominating influence leading to structure formation. Again it allows a fast fabrication.

3.5. A Special Method: Capillary Deposition

The capillary deposition method (CDM)[13,78,79] combines the advantages of several flow-induced deposition methods. In this method, colloidal spheres enter a planar capillary cell, which consists of two parallel glass plates that are separated by thin spacers, through a capillary tube that is attached to the bottom glass slide (Figure 10). Capillary forces drive the suspension into the cell and keep the liquid meniscus at the edge of the cell. Evaporation at these edges leads to a flow of suspension towards the edges. Because the spheres cannot leave the cell, they start to self-assemble at the open edges. The result is that the opal film grows with defined thickness towards the center of the cell.

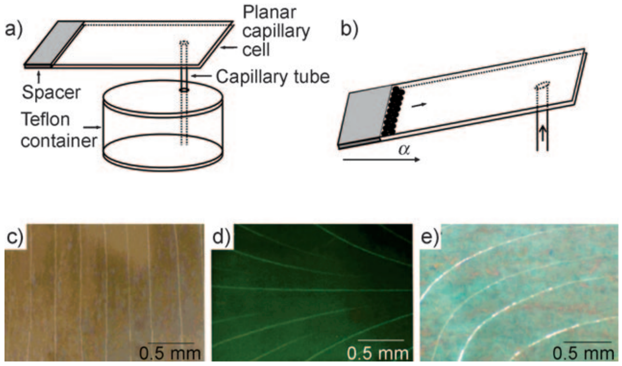


Figure 10. The capillary deposition method for stable colloidal suspensions (a) and the modification for suspensions with significant sedimentation (b). The resulting opal films have a defined cracking pattern. Near the edges it forms parallel lines (c), it becomes fan-like (d) along the centerline, and has curved regions (e). The cracks are nearly equidistant. (From Ref. [13])

The capillary deposition method can be used for a wide range of sphere sizes to make opal films that are effectively controlled by the spacer thickness. To form larger spheres, the planar capillary cell should be tilted to about 15° from horizontal to take advantage of the competition between sedimentation and flow-driven assembly in a controlled manner, and the suspension container should be continuously stirred (Figure 10).

Opal films made by this method have well-ordered parallel cracks aligned perpendicularly to the drying fronts. The macroscopic crack pattern can be controlled by modifying the open edges and the position of the entrance hole,[13] and by varying the solvent.[79] Furthermore, heterostructures consisting of stripes of opals with different sphere sizes can be achieved using this method.[78] Besides these possibilities, the resulting film is easy to handle and mechanically stable as long as it remains in between the supporting glasses.

The confinement cell method (Xia et al.)[51] and CDM are similar in that colloidal spheres are drawn into the cells and start to arrange near the edges, but a difference is in the suspension transferring technique. In the case of confinement cell, the transferring is due to external pressure, whereas in the case of CDM, the spontaneous pressure in a capillary is used. In both cases, the opal growth can be assigned to a flow-induced mechanism. In the confinement cell method, the edges comprise a microstructured membrane, whereas in CDM, the evaporation edges are open.

4. Opal Formation Mechanisms

Because of the large number of possible opal deposition methods, it is unlikely that there is only one single formation mechanism behind them. However, certain groups of methods are very similar, suggesting similar mechanisms. As we deal with three different driving forces in Figure 8, it seems appropriate to consider three different possible ordering mechanisms.

Experimental investigations of the mechanism of real, practical opal fabrication methods are rare. Often only model systems are studied which differ substantially from the opal deposition methods used. In principle the real formation process can either be investigated directly in situ, or an attempt can be made to understand the mechanisms by looking at the results of the formation, which may reveal aspects of the process which has occurred. Because the result of the process is always a densely packed fcc arrangement of spheres, only deviations from this ideal structure can reveal details about the underlying mechanism. These deviations are the different spontaneous defects (see Section 5). Different mechanisms are very likely to be connected with different kinds or concentrations of defects.

The more direct way of investigating opal formation, namely in-situ observation, is experimentally challenging. Wet colloidal crystals are quite often investigated, but real formation of the final dry opals has only been investigated in a few studies using UV/Vis spectroscopy,[80] normal microscopy,[81] and confocal microscopy[82,83] for selected deposition methods.

It is helpful to split the whole process of opal formation into five different partial processes, as shown in Figure 11. The different partial processes occur in every deposition method, but with different timescales and importance. They may occur sequentially in the whole sample or in parallel at different sample points.

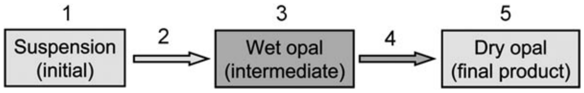


Figure 11. Partial processes of opal formation. The process starts with possible rearrangements in the suspension (1) and continues with the important phase transition from the disordered to the ordered state (2). Reconstructions of the formed wet opal may then occur (3). The drying begins with water removal (4), which can be followed by reconstructions in the dry state (5).

4.1. Field-Induced Deposition and Deposition by Volume Restriction

The changes in the suspension (step 1 in Figure 11) clearly occur in field-induced deposition methods, whereas they are much less important in the other deposition methods. The presence of gravity (or other external fields) results in a density profile in one direction, which can be measured by using light scattering or confocal microscopy.[84] The magnitude of the gravitational field is usually described by the Péclet number that relates the gravitationally induced drift to the thermal diffusion and indicates which effect dominates.[82] Small Péclet numbers indicate that the growth of the sediment can be considered as colloidal crystal growth from the supersaturated suspension just above the sediment, whereas a large Péclet number suggest that the gravitational force field strongly influences the colloidal crystal formation; this regime normally leads to badly ordered opals.

Supersaturation is reached at a point above a critical filling fraction of the suspension with spheres. For higher concentrations, the formation of an ordered solid is thermodynamically favored. This critical filling fraction depends on the potential between the spheres, but it can be expected that it is similar to that of hard spheres, which is 0.494.[85] In the deposition by volume restriction, crystal formation also starts after the critical filling fraction is exceeded. Thus, this group of methods is very similar to field-induced deposition at low deposition rates.

Not much is known about the subsequent rearrangement or drying processes. It is, however, clear that they strongly depend on the set-up geometry and external conditions.

Opal imitations for jewelry (see Section 2.3) are usually made by a sedimentation method. As mentioned above, they have a typical lizard-skin defect structure, which is very likely the result of column-like domains extending along the growth direction. This pattern is typical for sedimentation methods. We assign it to the process of competing growth at different regions leading to the different domains.

4.2. Flow-Induced Deposition

Several widely used methods to produce opals are classed as flow-induced deposition. Among these methods are vertical deposition and capillary deposition; both are based on the flow dragging the spheres as the solvent of the suspension evaporates at an evaporating front (meniscus). In both methods, the evaporating front and the colloidal growth front are found at different locations. As a consequence, the evaporating front has no decisive influence on the structure formation in process 2 (Figure 11).

The pressure from the meniscus produces a suspension flux and forces the particles to pack at the rim of the wet opal that has already deposited. It is understandable that a dense packing is formed there; however, the strong preference for cubic close packing (fcc structure) over hexagonal and random packing is somewhat surprising. This preference was hypothetically explained by Norris et al.[86] to be a result of the stronger (33 %) flow of solvent through "clear niches" (no sphere directly beneath them), leading to a higher deposition probability at these locations (Figure 12). This process would lead to a preferred ABC stacking. In general, the growth front may also have directions that differ from (111), but then similar mechanisms could also occur. The complete mechanism is however not yet fully understood and the current view assumes strongly simplified models.[87] Nevertheless, the proposal most likely contains the crucial idea for explaining the surprising and very useful property of opals produced by flow-induced methods, which is the strong domination of the fcc structure.

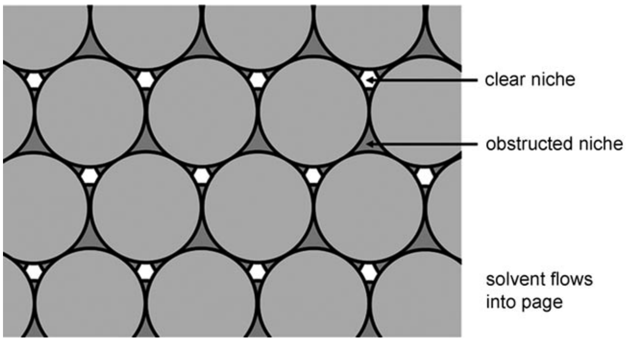


Figure 12. An attempt to explain the preferred fcc packing.[86] Although the static energetic differences can be neglected, the deposition on top of the clear niche is preferred, as the flow is stronger at this point.

As far as the wet opal deposition (process 2 in Figure 11) is concerned, see strong similarities are seen between vertical deposition and the capillary deposition method. In both cases, the transport of the particles to the crystal growth front proceeds by the suspension flow. However, in vertical deposition (see Figure 9), the evaporation front is very close to the growth front and they move together. In the capillary deposition method (Figure 10), the evaporation front is fixed at the cell edge, and it only starts to move after the suspension supply is stopped at the beginning of the drying. Therefore, in vertical deposition, all processes in Figure 11 proceed simultaneously, whereas in the capillary deposition method, deposition and drying occur at different times.

In wet opals, restructuring is likely (process 3 in Figure 11), but this process has not yet been investigated. However, a more detailed investigation of the drying and the post-drying processes (processes 4 and 5 in Figure 11) has been carried out[81] by following the changes of the transmission spectra during the drying process of the opal film. The capillary deposition method was used for opal preparation as it allows an easy separation between wet and dry opal formation processes. Although water loss happens during the first minutes after the start of drying, the Bragg peak and scattering background change over a longer timescale of some days. Not only the long-lasting Bragg peak shift is surprising, but also reversibility of the process during repeated drying, which suggests that the shifting of the Bragg peak is due to a proposed "physical sintering" rather than pure water loss or normal sintering. Based on the analysis of water loss, background changes, and Bragg peak shift, it became clear that the drying process consists of several phases before the crystal reach its final structure.

Information about opal formation processes 4 and 5 the can also be extracted from the shape of cracks occurring in every sample. These special defects are formed during drying of the already assembled wet opal,[13] and they can therefore give particular information about these partial processes. For example, the parallel cracks in the capillary deposition method point to an aligned drying front, whereas with undefined drying is observed in vertical deposition samples. The other defects should tell us more about the wet opal deposition (process 2), but they are much more difficult to investigate.

4.3. Natural Opals

The formation of natural opals is still a matter of surprising debate with a scientific, popular scientific, or even religious background. Sanders et al. suggested in their famous work that silica weathered from overlying rock percolates down through the rock mass to a cavity, where it is deposited and subjected to slow evaporation of the water.[23] However, the detailed processes of sphere formation and ordered sphere deposition are still unclear. After deposition, the space between the formed silica spheres is probably filled with hydrated amorphous silica, which hardens the mass by a long, continuous impregnation with soluble silica (cementing process).[42] This general picture mostly finds support in more or less similar manner.[24,88] However, considering the variety of opal occurrence, trace element distribution, and the degree of ordering in natural opals, it is not clear whether all natural opals are formed by a single mechanism or if different mechanisms can be assigned to different opal types. More systematic studies, including a representative selection of different opal sources (see, for example, reference [16]) are required to answer this question.

There are some interesting aspects that may be of importance in formulating a definitive theory of opal formation. First, there is no interconnection between the color play, atomic crystallinity (content of crystobalite and tridymite), and chemical composition (trace elements).[16] Second, natural opals occur with very different matrix materials. Third, it appears that no specific domain structure is typical for natural opals. Domain structures are always visible in natural opals, and they are very individual. In contrast, Gilson opals and other artificial opals formed by sedimentation show the so-called lizard-skin effect. This effect is a very specific domain structure and is used to distinguish between natural opals and imitations. Furthermore, it is a strong indication that natural opals are not formed by sedimentation.

It should be noted that often, only very particular stones are usually shown in publications. These opals are very expensive, rare, and thus by far not representative. Therefore, it is probable that these special examples are formed under exceptional conditions. The conditions under which these and normal opals form still remains a mystery.

5. Defects and Superstructures

5.1. Defect Classification and Description

Defects are, at a first glance, undesirable characteristics in opals and thus there is an initial desire to eliminate or at least minimize them. However, a closer look shows that they have the potential of being interesting functional features of the photonic systems, and have thus garnered much attention from experimentalists and theorists. For natural opals, defects form a part of their beauty.

In analogy to crystals, periodic structure in opals can be disturbed or interrupted, leading to many types of defects (see Figure 13). Defects can be classified in a similar way to those of atomic crystals.[89] However, defects in photonic crystals differ in many aspects from defects in such crystals owing to the absence of charge and the extremely short-range interactions between the spheres. As a result, distortions attributed to a single defect can appear in the lattice that extend much further than in atomic or molecular crystals. The defects include point defects, dislocations, stacking faults, domains, and cracks.

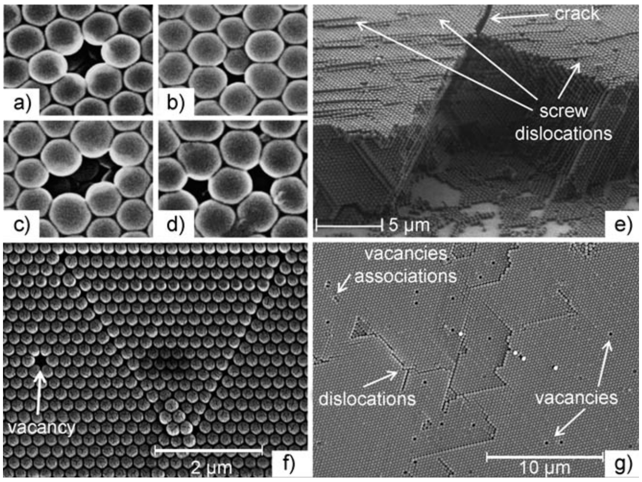


Figure 13. Examples of defects: Point defects: a) vacancy, b) Frenkel defect; c,d) vacancy associations; e) screw dislocations and a crack; f) screw dislocations running into the page and forming typical triangular features; g) typical overview of a (111) plane showing different defects (sedimented sample). The finite-length lines can be interpreted as the result of a section of the observation plane with ribbons penetrating this plane with a certain angle (likely 70.5°). Pictures from Refs [92] (a–d), [6] (e), and own results (f,g).

The simplest point defect is a lattice vacancy (Figure 13 a), or the absence of a sphere, which is also known as a Schottky defect. Owing to the lack of charge on the spheres, the need to attain electric neutrality is of little consequence in photonic crystals, and thus the missing sphere can be simply absent instead of being transferred from the interior to the surface as normally happens with atomic vacancies in crystals. Another point defect in photonic crystals is the Frenkel defect (Figure 13 b), in which a sphere is notably smaller than its neighbor and as a result it is displaced from its normal position in the fcc lattice. A third type of point defect that only occurs in photonic crystals is the presence of a sphere that is larger than its neighbors and alters the lattice ordering, thus inducing long-range distortions. In atomic crystals, alterations in bond lengths can compensate the local dislocations induced by larger atoms.

Dislocations are extended defects and they have been thoroughly studied in crystals. Slip, twinning, or growth effects produce displacements of crystallographic planes, giving rise to step or screw dislocations. An step dislocation is a type of defect in which an additional half-plane of spheres (or atoms) is present that distorts the lattice near the edge of the additional half-plane. Because the strength of interactions between the atoms in a crystal decay only slowly, such distortions can be rapidly compensated and the extent of the distortion is very restricted. Therefore, such a dislocation is a well-localized one-dimensional defect; that is, it consists of the edge of the additional half-plane. In photonic crystals, edge dislocations adopt a slightly different morphology, which is associated with the fact that the range of interaction among spheres is much shorter than in atomic crystals. Thus, the one-dimensional defect can extend further within the lattice, forming a finite-width ribbon. Such a ribbon appears as a line at an arbitrary section, as can be observed in many SEM pictures (for example, in Figure 13 g). In other words, the “edge” of an edge dislocation in photonic crystals has the width of several lattice constants. The extension of the “edge” thus gives the impression of a finite-length line. Screw dislocations in photonics crystals are similar to those seen for atomic and molecular crystals; examples are shown in Figure 13 e in which sphere planes form a spiral ramp wound around the line of the dislocation.

In analogy to atomic crystals with an fcc structure, partial displacements of the close-packed spheres planes in photonic crystals can produce stacking faults, which are typical two-dimensional defects and result in a mixture of fcc and hcp stacking. They are expected to be frequent.[90]

Domains can be considered as volume defects (three-dimensional defects) that can vary considerably in size. Figure 13 f shows a segregated domain of some tens of lattice constants. These typical triangular features are common in opal structures as segregated volumes, and probably result from local relaxation of the lattice owing to the stress introduced by combinations of edge dislocations. Much larger domains with different lattice orientations are also found in opals. Additionally, small volume defects can occur that include not only clusters of vacancies (Figure 13 c), but also local rearrangements. Such a situation has been reported for opals prepared by sedimentation. The internal stress caused by the empty volumes leads to disturbed regions in the lattice (Figure 13 d).

Cracks (see Figure 13 e, Figure 6 d, and Figure 10) can be formed upon shrinkage of the lattice during the drying of the wet ordered structure. Unlike crystals, the ratio between the crack widths and the crystal lattice constant in photonic crystals is much smaller, allowing the crack regions to be described as a disturbed part of the lattice with specific optical properties. Over short distances, they often follow the crystallographic directions (see, for example, Figure 6 d).

As far as the nature of the photonic band gap is concerned, defects can introduce localized photonic states in the gap, resulting in incoherent scattering and hopping-like photon transport, which is important for novel waveguides with low geometry restrictions.

Defects are spontaneously produced during opal formation; however, they can also be intentionally fabricated. These designed defect structures challenge not only creative engineering efforts, but also basic understanding and thorough characterization.

5.2. Spontaneous Defects

Spontaneous defects are an inherent property of all types of opals, and arise for a number of reasons. For instance, vacancies or localized lattice distortions can occur as a result of the use of non-monodisperse suspensions during opal preparation. Furthermore, defects are created during the self-assembly of the colloidal spheres for entropic reasons and owing to insufficient lattice optimization times (kinetic effect).

Different preparation methods can be expected to produce different kinds and numbers of defects. For example, flow-induced deposition methods (vertical deposition and capillary deposition) are reported to produce defect concentrations of about 0.01 per fcc elementary cell.[91] Other methods, such as sedimentation, can yield structures with one vacancy and one Frenkel defect per 50–100 fcc elementary cells.[92] Furthermore, although vacancy associations are not commonly found, bulk defects in the nature of local rearrangements (Figure 13 d) are rather frequent (about one per 100 fcc elementary cells).[92] These latter defects cause distortions in the close-packing in the range of 3–5 fcc elementary cells. Although stacking faults have been reported to be the most common defects in fcc structures,[90] in some preparations they, together with dislocations, appear to be uncommon.[92] Sedimentation has also resulted in orientation-disordered fcc domains, because ordered regions grow independently, and their meeting leads to the formation of disordered regions at domain boundaries.[92]

As cracks are normally formed upon shrinkage of the lattice during the drying of the wet ordered structure, they can have a different appearance according to the drying conditions and geometry of the set-up employed (see Section 3.5). However, cracks appear to be remarkably independent of other parameters, such as the nature of the spheres, dispersive media, or temperature. In particular, no change has been found in the direction of the cracking with change in growth temperature, despite temperature, of all preparation conditions, being identified as the most critical factor in the colloidal self-assembly of the spheres.[69]

5.3. Designed Defects

The possibility of creating defined structures inside a synthetic opal may be a key step towards applications in optics, for which a control of the propagation of light inside a photonic crystal is necessary. The design of intentional defects within the opals structures has been ingeniously addressed by employing various approaches, including randomly-spread defects,[93] local refractive-index modification,[94] multilayers,[95] substrate-defined defects,[96] electron-beam lithography,[97] photolithography,[98,99] multiphoton polymerization,[100] direct laser writing with pulsed UV F_2 lasers[101] and Ti:sapphire lasers,[102] electron beams of SEMs,[103] and focused ion beams.[104]

All these attempts mainly deal with the technical difficulties of the high-precision nanostructuring. Braun and coworkers[100] have managed to overcome fabrication challenges and have produced an operating defect-based device. They made a complete-band-gap photonic crystal consisting of a silicon inverse opal modified by incorporation of three-dimensional defects that guided NIR light along the defects (Figure 14). The demonstration of this important functionality significantly improves the capacities of photonic crystals.

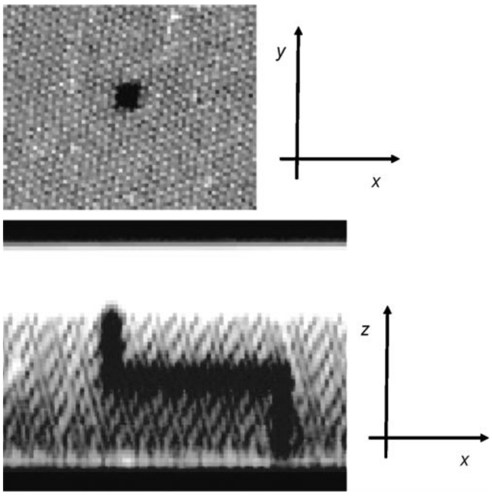


Figure 14. Confocal microscopy images of a designed three-dimensional defect structure that forms a doubly bent wave guide.[100]

An interesting special defect is an artificially introduced thin layer between opals, which is often called a planar defect. The matching of the defect with the lattice structure is conceptually easy and has indeed been successfully achieved. This matching is important because only a nearly undistorted host lattice will ensure a defined optical function. Layers of different compositions and functionalities have been embedded within opaline structures using several creative approaches. Among them, monolayers of spheres of an arbitrary diameter were introduced between two opal structures by the Langmuir–Blodgett technique,[105–107] a silica slab between two inverted opal layers was fabricated using chemical vapor deposition,[108,109] and polyelectrolyte multilayers were incorporated between two opals. The last example allows access to optically transmitting states within the frequency range of a photonic band gap; the states were tunable by gas adsorption[110] or by reactions of bound ferrocene units.[111]

5.4. Superstructures

Disturbances of the lattice that are much smaller than the dominating lattice are normally called defects. Large-scale disturbances can form different, extended regions in the crystalline system, and these disturbances are called superstructures or domains. Figure 15 shows an example in which opal films consisting of different colloidal crystal strips have been formed by the capillary deposition method.[78] These opal superstructures show multiple stop bands in optical transmission and reflection, and show promise for applications in integrated optics and microdevices.

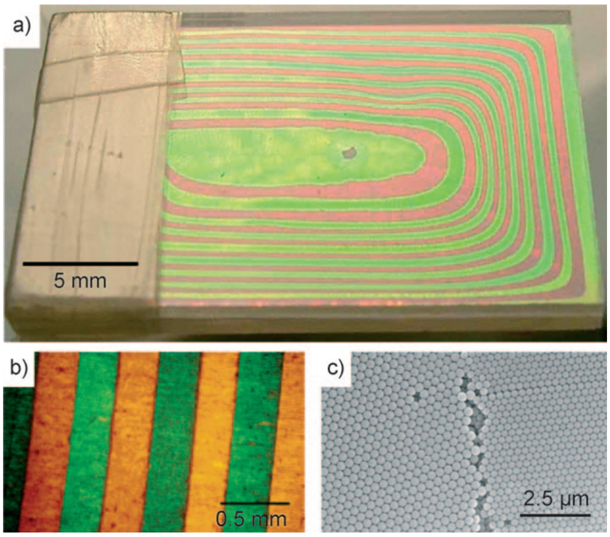


Figure 15. Example of a superstructure: a) Photograph of an alternating strip opal consisting of 12 strips of colloidal crystals; b) Optical microscopy image of such a structure in transmission; c) SEM image of a boundary region of two adjacent colloidal crystal strips.[78]

6. Opal Modification

6.1. General Remarks

In principle, opal structures can be formed for all chemical compounds, but opal fabrication is limited in practice to small spheres that can be produced in a monodisperse distribution. To date, this is only possible for silica and some polymers (polystyrene, PMMA, and certain block copolymers). Furthermore, the opal band structure is only of limited interest; that is, artificial opals do not have a complete photonic band gap, thus excluding them from a number of potential applications. This incomplete band gap is due to the low refractive index contrast of the current materials and the high space-filling factor of the opal structure. In an ideal opal, 74 % of the space is filled with optically dense material.

The limited applicability of pure opals has led to several attempts to modify them. Simple modifications are sintering and fillings to give the opals higher stability and additional functionality. However, the most important modification is inversion leading to inverse opals (also called inverted opals or opal replicas). In this structure, both above-mentioned drawbacks of opals can be avoided. Opal inversion is possible for a variety of possible chemical systems (see, for example, reference [112]), and most importantly, inverse opals can have a complete band gap.

Calculations show that surprisingly, inverse structures consisting of air spheres in a medium have a complete band gap above a critical refractive index contrast ($n \geq 2.85$). The gap occurs between the eighth and the ninth band in the band structure and should have a width of about 5% for a silicon inverse opal. This prediction initiated a huge number of investigations to attempt to realize such structures by infiltration of a highly refractive material followed by template removal using dissolution or calcination. For several years, this was one of the most studied topics of photonic crystal research. Inverse opals with a complete band gap are in principle now available, even though only one specific complete band gap effect has yet been shown (see Section 7.4). It is likely that the defects in these structures often destroy the complete band gap effects. Nevertheless, a decisive step has been made and the research has produced a large number of highly useful techniques for opal modification: sintering, filling, and inversion.

Sintering of opals forms necks between of the spheres, which allows the available pore size to be tuned and the mechanical strength of the opal to be improved. This neck formation is useful, for example, in subsequent inversion by avoiding sphere separation during infiltration. Additionally, the necks ensure interconnection of the inverse opal pores thus formed by producing windows between the empty spheres, which allows the interpenetration of substances and in particular the removal of the templates. In one example, polystyrene opals were heated to 80 °C for 30 minutes prior to titania precursor infiltration.[113]

Fillings have been considered theoretically by Busch and John.[3] Apart from looking at the effect of fillings on the photonic bands, they also proposed the use of liquid crystals to make the opals switchable. Such systems have been successfully realized.[114] If precursor molecules are used, filling the opal is a necessary initial step for inversion. This filling can be achieved in the gas or liquid phase, and the technique will be discussed more in detail in the next section.

6.2. Inversion

The intensive search for highly refractive inverse opals having a complete band gap started after the work of the groups of Velev,[115] Imhof,[116] Holland,[117] Zakhidov,[118] and Wijnhoven.[53] Since then, a variety of methods for infiltration has been proposed, such as chemical vapor deposition (CVD),[48,119–121] atomic layer deposition (ALD),[122,123] liquid-precursor infiltration,[53,116,117,124,134] co-assembly processes,[125] and electrochemical deposition.[126,127] Some of these methods (CVD and ALD) have been adapted from industrial semiconductor processing and therefore fit in well with these technologies.

After infiltration of the opal with high-refractive-index materials, a selective removal of the opal template follows. This can be achieved by treatment with HF for silica opals, or organic solvents (dichloromethane, toluene, or acetone) or calcination for latex opals.

6.2.1. Chemical Vapor Deposition

In CVD, gaseous precursor molecules of semiconductor materials (Si, Ge, InP, GaP, etc.) are transformed into a nanometer-thin layer of solid material on surfaces. The amorphous solid so formed between spheres (usually silica, which resists high temperatures) is then annealed to form polycrystalline structures. This method has been successfully used to create a three-dimensional silicon photonic crystal with a complete band gap at a wavelength of 1.5 μm (Figure 16).[119] The nearly conform nature of low pressure CVD[120] has been used to improve the quality of the inverse opals.

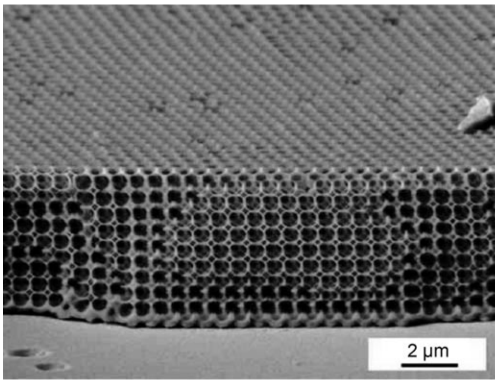


Figure 16. Silicon inverse opal from a silica opal template formed by CVD. Si_2H_6 was used as the precursor gas, which was decomposed on the sample at a temperature of 375 °C. The resulting amorphous semiconductor was crystallized afterwards by a annealing at 600 °C.[120]

6.2.2. Atomic Layer Deposition

ALD is a modification of CVD, and can be used to deposit monolayer films. This self-limiting process consists of repeated saturated steps involving pulsing precursors, which results in an atomic monolayer on the previous layers. For II–VI or III–V films, a metal precursor (such as $ZnCl_2$) is pulsed into a process chamber, where it is chemisorbed on the surface of the substrate, followed by a purge step to remove any non-chemisorbed precursor. Thereafter, a nonmetal precursor (such as H_2S) is applied in a similar manner. This nonmetal gas also chemisorbs on the surface and undergoes a reaction with the atomic metal layer already deposited. The process is then repeated layer-by-layer. Using this method, TiO_2, ZnS, and tungsten nitride[128] inverse opals were successfully obtained.

6.2.3. Liquid Precursor Infiltration

This method is often differentiated into infiltration with molecular precursors, sols, or nanoparticle suspensions. However, these methods have strong technical similarities and similar difficulties. If solutions of precursor molecules are used[53,134] these precursors are transformed into solids by an intra-opal sol–gel process after hydrolysis. Alternatively, a sol can be formed before infiltration, and the sol–gel process is then completed inside the opal.[113] The third alternative is a complete separation of nanoparticle synthesis, their infiltration, and then subsequent transformation of the nanoparticles to the solid, forming the inverse opal.

The first two techniques are very versatile and have resulted in the synthesis of various metal oxide structures, such as SiO_2, TiO_2, ZrO_2, Al_2O_3, Y_2O_3, TiO_2-ZrO_2, and Y_2O_3-ZrO_2.[34,53,117,129,130] In many cases, the whole process (infiltration, hydrolysis, condensation, and drying) must be repeated several times to ensure that the voids are sufficiently filled. The drawback of this method, and in particular for titania, is a considerable degree of roughness (ca. 10 nm), low filling fractions (about 12% because the solvent necessary for the sol–gel process occupies some space), and a large volume loss (shrinkage of 10–40%).

The use of pre-prepared nanoparticles with a size of about one-tenth of the void channel diameter of the opals offers more flexibility in the choice of the chemical composition of the inverse opal, whilst at the same time reducing the degree of shrinkage, as nanoparticles are in their final chemical form. CdS nanoparticles have for example been used for such a purpose.[131]

6.2.4. *Co-Assembly*

A special form of nanoparticle incorporation is the co-assembly of opal spheres and nanoparticles (see, for example, reference [125] and also in reference [7]). The small nanoparticles are dragged to the solvent-evaporating front by capillary forces and fill voids between colloidal spheres assembling there. Drying the mixture by controlled evaporation of the solvent in a chamber with high humidity leads to the formation of a colloidal crystal of spheres with nanoparticles in the voids; deposition and infiltration occur simultaneously.[125]

6.2.5. *Electrochemical Pore Filling*

The electrochemical pore filling[126,127] technique is an effective route to obtain high-density filling of the interstices between the spheres of opal with metals. The growth rate of the material is easily controlled by the electric current. This method typically produces residual volume structures instead of shell structures (see Section 6.3). This feature, combined with dense and continuous nature of the walls, which are already in their final chemical form, results in high mechanical stability and very small shrinkage. The method has successfully been used to infiltrate opals with CdS and CdSe.

6.3. *Inverse Opal Tuning*

The term “inverse opal” suggests a straightforward system: an opal with inverted refractive index contrast. However, this is usually not the case and an oversimplification; the chemical inversion process has a much higher flexibility than a simple mathematical inversion. It turns out[130,132] that three different basic structures can result after inversion: 1) a residual volume structure (RVS), in which the infiltrating medium completely fills the entire space among the opal spheres; 2) a shell structure (ShS), consisting of thin layers around the original opal spheres; and 3) a skeleton structure (SkS) filling the interstitial voids between the opal spheres, with rod-like parts forming a network.

Interestingly, these structural variations have a dramatic effect on the band structure. Whereas the first two structures, RVS and ShS, can only have a tunable band gap between the eighth and the ninth band, the skeleton structure can have a band gap between the fifth and the sixth band (Figure 17).

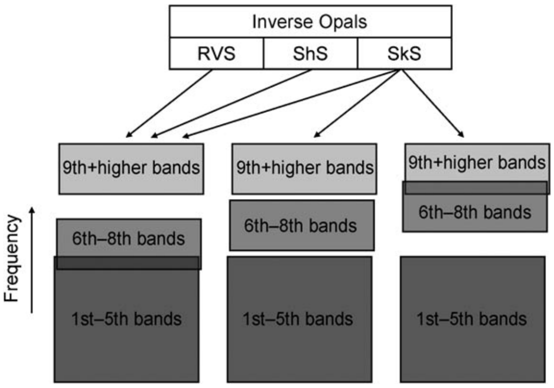


Figure 17. The different types of inverse opals and the related photonic band structures.

The existence and width of the band gap can be tuned by the diameters of the rods and effective refractive index of the skeleton-forming material. By applying coating methods, such as CVD or ALD, these two parameters can be varied and the band-gap properties can thus be manipulated still further.

Tuning of the shell structures is also easily carried out. Interestingly, multilayer structures have been achieved with high precision by the means of CVD.[133] This technique enables efficient fine-tuning of shell composition and thickness. The window size of the shell structures can be adjusted by sintering prior to inversion. The sol–gel method allows the porosity of both the shell structure and the skeleton structure to be varied.[134,135]

7. Properties and Selected Applications

7.1. *Opalescence*

In the field of photonic crystals, the word opalescence is used to designate a very characteristic property of many nanostructured systems, namely the dependence of the spectral reflection or transmission band on the viewing angle. In simpler terms, this property describes the occurrence of angular-dependent brilliant colors (that is, narrow bands in the spectra). However, the usage of this word varies in different scientific communities. In mineralogy, opalescence has been used[26] for a long time, partially with the same meaning,[24] partially with a wider meaning that includes all angular-dependent optical effects (also arising from scattering),[17] and also to indicate simply a milky appearance, or scattering effects.[24,17,18] Unfortunately, the noun and the corresponding adjective (and even the verb in German[136]) can refer to different properties (see, for example, references [24] and [17]).

Iridescence is sometimes used as a synonym of opalescence. However, some researchers use iridescence to describe interference phenomena at thin layers,[137] regardless of how pronounced the spectral features are. In multilayer systems, it is equivalent to opalescence. Among minaralogists,[17] the word iridescence appears to be seldom used in connection with opals. Other synonyms sometimes used for opalescence are play-of-color[17] or fire.[18]

7.2. Applications of Color Effects

As one of the most important properties of photonic crystals, opalescence has many applications that range from decoration to devices requiring the display of colors. Decoration applications perhaps first come to mind as they are closely related to the color effects of photonic crystals.[6] In some cases,[138] a huge alteration in color can be achieved by changing the viewing angle to greater than 40° with respect to the position of the light source. In another work,[30] a large number of opalescent microparticles were prepared from colloidal suspensions drying on hydrophobic surfaces. Besides the normal tuning possibilities, the incorporation of small metallic nanoparticles in the lattice of these objects was studied that help to enhance the diffraction color by increasing the reflectance. In recent years, both large and small companies (for example, Merck and Opalux) have undertaken steps to commercialize opal products for decoration applications and for devices using opalescence.

Devices that are based on the color effects of opals and inverse opals can be found in applications spanning from purely inorganic to bioorganic. Opalescence has been used for displays,[139] photonic inks,[140] switches or sensors,[141,142] in biometric recognition devices,[143] drug-release or drug-resorption monitoring architectures,[144] and glucose sensors.[145]

For displays, opalescence enables one pixel to show various bright colors. One current approach[139] is based on the swelling of an inverse opal, which is a relatively slow process, and thus restricts the application range, but is nevertheless of importance for electronic paper and displays that change slowly. The development of materials known as "photonic ink"[140] allows the reflection of bright and narrow bands of color. Additionally, because such photonic ink only requires low voltages for switching between different wavelengths, it is becoming increasingly more attractive in applications as energy saving devices.

Simple indicator systems for tensile strain can be constructed based on the color change that arise from the shift of the reflection band of the photonic crystal (Figure 18a).[141] Deformation of the lattice can also be achieved by swelling in carbon disulfide, which has applications in chemomechanical sensing.[142]

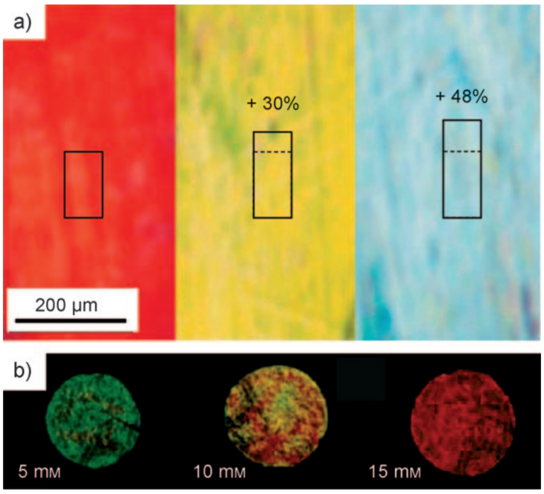


Figure 18. a) Observed color of a polymeric photonic crystal at normal incidence and at different tensile strain levels. Red: without strain (left); yellow: at a length extension of 30% (middle); light blue at a length extension of 48% (right).[141] b) Color changes of a chemically responsive inverse opal as a function of the degree of swelling owing to an increase in glucose concentration: green at 5 mM (left), yellow at 10 mM (middle), and red at 15 mM (right).[145]

Elastomeric void photonic crystals integrated with a camera have been assembled and used to obtain the characteristic fringes of fingerprints.[143] These systems are based on structural changes caused by the pressure imprinted by the finger on the device, which provokes a shift in the reflection band of the photonic material. A color map of the pressed area yields a picture with enough resolution to resolve line ridges on the skin.

Applications in the field of human tissues are also based on chemical processes occurring in the pores of the materials. For example, shifts of spectral peaks have been found to correlate with the partial pressure of condensable vapors, such as ethanol or hexane, or with the concentration of impregnated caffeine.[144] In these cases, the monitoring of the concentrations of different compounds even through 1 mm thick human hand tissue has been successfully achieved, thus illustrating the sensitivity of the photonic systems in vivo. Furthermore, colorimetric sensors for glucose in blood are attractive devices, which use the swelling of the lattice that occurs when glucose is chemically bound to suitable functional groups (Figure 18b).[145]

7.3. Emission Tuning and Laser Resonators

The influence of photonic crystals on spontaneous emission has stimulated research for some time. This important effect has basic-research and application aspects. The first use of colloidal crystals for emission tuning dates back to 1990.[146] Inhibition of dye emission was shown by measurements of the lifetime of an excited electronic state, thus proving the influence of the nanostructure on the density of photonic states. Later the effect was also shown for semiconductor quantum dots and rare earth complexes embedded in opals (see, for example, [147]).

Apart from the influence of photonic crystals on the emission rate, their influence on the angular characteristics of the emission is highly interesting, especially as far as applications are concerned. Anisotropic emission has been recently studied for dye-doped opals, for example in reference [55]. The use of opals for emission tuning of LEDs is a particularly interesting area because there is a strong pressure to reduce the costs of these devices. A self-assembly method could be a good alternative to a microstructuring method to achieve the same effect.

The coupling of exited states to special modes in photonic crystals is also the basis for much research into photonic micro- and nanolasers (see, for example, reference [148]). Opal fabrications often involve simple handling techniques, which appear to be technologically attractive for applications in such fields.[149]

7.4. A Complete Photonic Band Gap

An interesting race was underway in the 1990s to achieve a complete photonic band gap, but since then it has changed into a relatively silent research area. A claim has been made of a complete band gap for silicon-based inverse opals; however, the evidence was not totally convincing, and reliable fabrication seemed to be a problem.

In 2000, Blanco et al.[119] prepared a good-quality silicon inverse opal for the first time and demonstrated that the reflectance spectrum had maxima in the required frequency ranges. However, the height of the maxima differed by up to 20% from the 100% predicted by theory. Experimental inaccuracy could explain this deviation, but the disparity made their argument for the complete band gap weak. Furthermore, the question arises as to whether such results, even with a good agreement to theory, are complete evidence of a full band gap. Nevertheless, this work was the first strong hint that a complete band gap is achievable. Vlasov et al.[120] analyzed reflectance spectra with higher precision using a microscope spectrometer that limited their experimental error to about ±5%. As a result, they could show that the reflectance in the expected band-gap region is larger than 95%. The authors also remarked about some reproducibility problems with the spectra, which might be connected with domains of different orientation in the photonic crystal or with regions with different silicon content.

Convincing evidence of the complete band gap required greater preparation efforts, and was published eventually in 2008. Braun et al. used inverse opals that should have complete band gaps according to calculations, and inscribed three-dimensional defect waveguide structures into them (see Section 5.3).[100] They showed that these photonic structures indeed work, which would only be the case if the complete band gap was achieved. This nice result also illustrates the way towards a technological use of these materials and should reactivate the research on opal-based complete-band-gap materials.

7.5. Slow-Photon Effects

Among the many interesting properties of photonic crystals, slow light propagation is one of the unique properties of these crystals that is not exhibited by other materials.[150] Moreover, it is expected to be relatively insensitive ("robust") to lattice disturbances, making it especially interesting for opals. Because of the photonic band structure, light can propagate with extremely low group velocities at specific frequencies.[151–153] This effect is of basic and practical interest, as it can enhance non-linear optical interactions, laser efficiencies, sensor efficiencies, and the photochemical activity of materials.[154]

In media with refractive index n, the speed of light propagation, or more correctly the phase velocity v_p is given by $v_p = \omega/k = c/n$, where k is the wave number of the light with angular frequency ω. The velocity of an electromagnetic pulse propagation is, however, different from v_p, and is determined by the group velocity v_g [Eq. (1)].[155]

$$v_g = \frac{\partial\omega}{\partial k} = c\left(n + \omega\frac{dn}{d\omega}\right)^{-1} \tag{1}$$

In normal media, there are only slight differences between both velocities, but in photonic crystals the situation alters dramatically, and v_g can be much smaller than v_p. This is a result of the band structure $\omega(k)$, or after recalculation, the strong dispersion $n(\omega)$ of these media. Slow photons are defined as being when $v_g \ll c$, independent of the value of the phase velocity. In some cases, v_g can even be zero. In photonic crystals, the slope of the bands $\omega(k)$ decreases when approaching the band edges, that is, the derivative of $\omega(k)$ tends to zero. This means that the group velocity is considerably reduced when approaching band gaps (Figure 19).

The practical applications of slow light are based on the possible strong enhancement of light–matter interactions, such as absorption and nonlinear effects. Such an enhancement can be used in optical delay lines, phase shifters, optical microamplifiers, and microlasers.[156] Apart from these applications, which are currently being adopted in two-dimensional photonic-crystal waveguide slabs for telecommunication purposes, there is also endeavors to use the slow photons in three-dimensional photonic crystals,[157] and in particular for the enhancement of photochemical processes.[158]

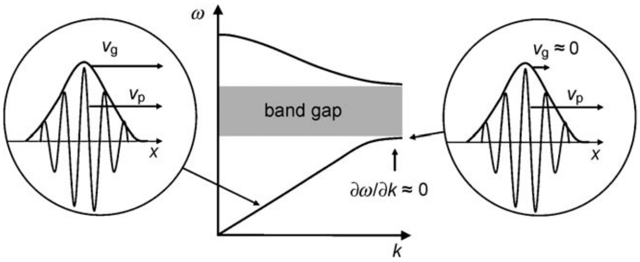


Figure 19. Electromagnetic pulse propagation in photonic crystals. Near the center of the Brillouin zone, light travels with $v_g \approx v_p \approx c/n$ as usual. At photon energies approaching a band gap (partial or complete), the group velocity decreases and approaches zero.

Photochemical processes are used in photovoltaic devices and photochemical reactors. Enhancing them would increase the device performance, and slow photons are a possible route. For opals and inverse opals, the group velocity will be clearly reduced near to the (complete or partial) gaps. However, the application is impeded by the requirement of high-quality materials.[159]

An approach to achieving slow photon effects with photocatalysts was published by Ozin et al.[158] They fabricated an inverse opal of the photocatalyst TiO_2 by infiltration of an opal mold. This photocatalyst has been thoroughly investigated, and it has the additional advantage of a relatively high refractive index, which promises strong photonic effects. The frequency of the photonic stop band, and thus also of the slow photons, was tuned with respect to the semiconductor electronic band gap to efficiently use the slow photons so arising for a photochemical reaction. The photodegradation of the dye methylene blue adsorbed on the TiO_2 inverse opal was probed under different irradiation conditions. The measurements indicate an almost two-fold enhancement of the decomposition rate when the irradiation wavelength overlaps with the expected slow-photon wavelength in this structure. Angle-dependent photodegradation measurements were also carried out, and they showed an angular sensitivity, which supports the slow-photon interpretation of the measured enhancement.

The relatively low photochemical enhancement factor can be ascribed to sample imperfections and to enhanced reflection of light in the slow-photon region wavelength region. There is always competition between slow-photon enhancement and enhanced reflectivity near the stop band. It has been suggested that the interplay between the photonic band structure and the absorption in TiO_2 can favor the first effect over the second. It is also worth considering whether higher-order bands with a low group velocity at the TiO_2absorption edge can be used to increase the total photocatalytic efficiency, as they might behave differently from the first-order stop band.[158]

Apart from the slow-photon technique, there is a much simpler approach to enhance photovoltaic efficiencies, which is based on scattering and reflection from the photonic crystal structure. The photocurrent of solar cells can be increased by coupling a photonic crystal to a conventional photoelectrode. The photonic crystal can thereby play two roles: as a dielectric mirror for wavelengths corresponding to the stop band, and as a medium for enhancing light absorption on the long wavelength side of the stop band.[157]

For visible-light and UV-light wavelengths, scattering can become a dominant factor because fabricated three-dimensional photonic crystals will always have defects. The opal self-assembly methods generate a lot of defects, as shown in Section 5. Bearing this in mind, slow-photon effects might be of special interest because they can tolerate many defects. Highly ordered photonic crystals are desirable but not absolutely necessary for practical applications.[160]

8. Summary and Outlook

Opal research is an active and wide field. There are about 1000 papers with direct reference to artificial opals in the literature, but in the enormously large fields of colloidal crystals and photonic crystals, a large number of opal-related works have been published without direct reference to them. Nevertheless, these papers have a strong influence on opal research. The large number of relevant publications has required a rigorous selection, which is unfortunately subjective. Our selection was driven by a wish to highlight the biggest challenge we see in this field: the defects. Decisive progress in the field will strongly depend on a good understanding and control of the opal defects.

The role of opals as a prototype for self-assembled photonic crystals is fulfilled in an excellent manner. The self-assembly approach to photonic crystals functions efficiently, many variations are possible, and fine control is becoming increasingly more possible. The power of the self-assembly approach is shown by examples from nature, where many similar and varied systems are observed in the natural opals.

As far as opals as a prototype for the realization of photonic band structure effects in structured matter is concerned, a more critical consideration is required. To date, there are only a few examples of artificial opals or related systems that have non-trivial band structure effects and are useful alternatives to photonic crystals fabricated by the top-down approach. The latter approach has produced impressive examples, with applications in photonic experiments and device-like set-ups. For the opal and inverse opal systems, it has required long-term efforts to achieve structures that are useful for practical devices. However, artificial opals still contain too many spontaneous defects, making their use difficult. The mean free path for the photons in artificial opals is seldom longer than 10 μm. Inscription techniques to make functional structures in opals have made impressive progress; however, they still need improvement. Nevertheless, we believe that the inherent drawbacks of the top-down photonic-crystal samples (difficulties making them large, cheap, and thick) are also very problematical. Indeed, much competition between the top-down and the bottom-up approaches can be expected for the realization of devices based on photonic crystals.

Apart from the application in information processing systems, attempts have been initiated to find so-called robust applications of photonic crystals; that is, those applications that can tolerate high defect concentrations. One of the most important applications of this kind is surely the enhancement of photochemical effects by slow light. However, whether slow light (low group-velocity states) is really insensitive to certain kinds of lattice disorder has still to be shown. Effects similar to those used for improvement of photocatalysis could also enhance photovoltaic cell efficiencies.

The general problem regarding the conceptual and practical integration of opals into devices that has been mentioned in earlier works[4,5] has not totally been solved but it has been reduced, and it exists only for applications in information-processing systems. A device concept can only be made based on the availability of a suitable defect-inscription technique.

Finally, another long-standing problem is the question of opal perfection, or in other words, spontaneously generated defects. Although it is generally known, the problem has been ignored somewhat, possibly because impressive results have been obtained with the current opals. Now, it seems timely to resolve this non-trivial and crucial problem as well.

We thank A. Lehmann for the German translation of the manuscript, Dr. R. Goddard for a very carefully proof-reading and many substantial hints, and F. Schüth and the anonymous referees for valuable remarks. The International Max Planck Research School SurMat is thanked for financial support.

Received: January 13, 2009

---

[1] J. D. Joannopoulos, R. D. Meade, J. N. Winn, *Photonic Crystals: Molding the Flow of Light*, Princeton University Press, **1995**.

[2] H. S. Sözüer, J. W. Haus, R. Inguva, *Phys. Rev. B* **1992**, *45*, 13962.

[3] K. Busch, S. John, *Phys. Rev. E* **1998**, *58*, 3896.

[4] Y. Xia, B. Gates, Y. Yin, Y. Lu, *Adv. Mater.* **2000**, *12*, 693.

[5] "Materials Aspects of Photonic Crystals": C. Lopez, *Adv. Mater.* **2003**, *15*, 1679.

[6] B. Lange, F. Fleischhaker, R. Zentel, *Phys. Status Solidi A* **2007**, *204*, 3618.

[7] D. Wang, H. Möwald, *J. Mater. Chem.* **2004**, *14*, 459.

[8] A. R. Parker, *J. Opt. A* **2000**, *2*, R15.

[9] S.-M. Yang, S. G. Jang, D.-G. Choi, S. Kim, H. K. Yu, *Small* **2006**, *2*, 458.

[10] U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, D. A. Weitz, *Science* **2001**, *292*, 258.

[11] H. Guo, T. Narayanan, M. Sztuchi, P. Schall, G. Wegdam, *Phys. Rev. Lett.* **2008**, *100*, 188303.

[12] P. Schall, D. A. Weitz, F. Spaepen, *Science* **2007**, *318*, 1895.

[13] H. L. Li, W. Dong, H. J. Bongard, F. Marlow, *J. Phys. Chem. B* **2005**, *109*, 9939.

[14] M. Okrusch, S. Matthes, *Mineralogie*, 7th ed., Springer, Berlin, **2005**.

[15] M. A. S. Kalceff, M. R. Phillips, A. R. Moon, A. Smallwood, *Phys. Chem. Miner.* **1997**, *24*, 131.

[16] E. Gaillou, A. Delaunay, B. Rondeau, M. Bouhnik-le-Coz, E. Fritsch, G. Cornen, C. Monnier, *Ore Geol. Rev.* **2008**, *34*, 113.

[17] A. W. Eckert, *The World of Opals*, Wiley, New York, **1997**. The book gives an impressive overview of mineralogical aspects of opals. Unfortunately the theories on opal formation are obscured by personal stories, and there are contradictions between the meaning of "opalescent" (p. 380) and "opalescence" (p. 387, note 1.3).

[18] K. Nassau, *Gems Made by Man*, Chilton Book Company, **1980**.

[19] C. V. Raman, A. Jayaraman, *Proc. Indian Acad. Sci. Sect. A* **1953**, *101*, 343.

[20] J. V. Sanders, *Nature* **1964**, *204*, 1151.

[21] J. B. Jones, J. V. Sanders, E. R. Segnit, *Nature* **1964**, *204*, 990.

[22] J. V. Sanders, Diffraction of Light by Opals, *Acta Crystallogr. Sect. A* **1968**, *24*, 427.

[23] P. J. Darragh, A. J. Gaskin, B. C. Terrel, J. V. Sanders, *Nature* **1966**, *209*, 13.

[24] C. Weise, *Opal. Extra-Lapis No. 10*, C. Weise-Verlag, München, **1996**.

[25] A. P. Philipse, *J. Mater. Sci. Lett.* **1989**, *8*, 1371.

[26] a) T. Ruhl, G. P. Hellmann, *Macromol. Chem. Phys.* **2001**, *202*, 3502; b) T. Ruhl, P. Spahn, H. Winkler, G. P. Hellmann, *Macromol. Chem. Phys.* **2004**, *205*, 1385.

[27] W. Ebeling, R. Feistel, *Strukturbildung bei irreversiblen Prozessen*, Akademie-Verlag, Berlin, **1982**.

[28] Z. Li, J. Wang, B. Gu, *J. Phys. Soc. Jpn.* **1998**, *67*, 3288.

[29] T. Ruhl, P. Spahn, G. P. Hellmann, *Polymer* **2003**, *44*, 7625.

[30] V. Rastogi, S. Melle, O. G. Calderón, A. A. García, M. Marquez, O. D. Velev, *Adv. Mater.* **2008**, *20*, 4263.

[31] R. Anselmann, H. Winkler, *Adv. Eng. Mater.* **2003**, *5*, 560.

[32] J. Park, J. Moon, H. Shin, D. Wang, M. Park, *J. Colloid Interface Sci.* **2006**, *298*, 713.

[33] K. Wostyn, Y. X. Zhao, G. de Schaetzen, L. Hellemans, N. Matsuda, K. Clays, A. Persoons, *Langmuir* **2003**, *19*, 4465.

[34] B. T. Holland, C. F. Blanford, T. Do, A. Stein, *Chem. Mater.* **1999**, *11*, 795.

[35] Sh. H. Kim, J. M. Lim, W. Ch. J. , D. G. Choi, S. M. Yang, *Adv. Mater.* **2008**, *20*, 3211.

[36] S. M. Yang, G. Ozin, *Chem. Commun.* **2000**, 2507.

[37] P. Ferrand, M. J. Minty, M. Egen, J. Ahopelto, R. Zentel, S. G. Romanov, C. M. Sotomayor Torres, *Nanotechnology* **2003**, *14*, 323.

[38] A. M. Kapitonov, *Photonics Nanostructures Fundamentals Applications* **2008**, *6*, 194.

[39] M. Tymczenko, L. F. Marsal, T. Trifonov, I. Rodriguez, F. R. Manzano, J. Pallares, A. Rodriguez, R. Alcubilla, F. Meseguer, *Adv. Mater.* **2008**, *20*, 2315.

[40] A. S. Dimitrov, K. Nagayama, *Langmuir* **1996**, *12*, 1303.

[41] See e.g.: J. C. Hulteen, R. P. Van Duyne, *J. Vac. Sci. Technol. A* **1995**, *13*, 1553.

[42] "Formation of Precious opal": R. K. Iler, *Nature* **1965**, *207*, 472.

[43] K. E. Davis, W. B. Russel, W. J. Glantschnig, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 411.

[44] H. Míguez, F. Meseguer, C. Lopez, A. Mifsud, J. S. Moya, L. Vazquez, *Langmuir* **1997**, *13*, 6009.

[45] A. L. Rogach, N. A. Kotov, D. S. Koktysh, J. W. Ostrander, G. A. Ragoisha, *Chem. Mater.* **2000**, *12*, 2721.

[46] M. Holgado, F. García-Santamaría, A. Blanco, M. Ibisate, A. Cintas, H. Míguez, C. J. Serna, C. Molpeceres, J. Requena, A. Mifsud, F. Meseguer, C. López, *Langmuir* **1999**, *15*, 4701.

[47] A. van Blaaderen, K. P. Velikov, J. P. Hoogenboom, D. L. J. Vossen, A. Yethiraj, R. Dullens, T. van Dillen, A. Polman in *Photonic Crystals And Light Localization In The 21st Century* (Ed.: C. M. Soukoulis), Kluwer, Amsterdam, **2001**, pp. 239–251.

[48] M. Müller, R. Zentel, T. Maka, S. G. Romanov, C. M. S. Torres, *Adv. Mater.* **2000**, *12*, 1499.

[49] Q. Yan, Z. Zhou, X. S. Zhao, *Langmuir* **2005**, *21*, 3158.

[50] P. Jiang, J. F. Bertone, K. S. Hwang, V. L. Colvin, *Chem. Mater.* **1999**, *11*, 2132.

[51] Y. Xia, B. Gates, S. H. Park, *J. Lightwave Technol.* **1999**, *17*, 1956.

[52] P. Gilson. No direct publication is known, but Gilson gave quite detailed information to others, and especially to Nassau. See reference [18].

[53] J. E. G. J. Wijnhoven, W. L. Vos, *Science* **1998**, *281*, 802.

[54] C. Fustin, G. Glasser, H. W. Spiess, U. Jonas, *Langmuir* **2004**, *20*, 9114.

[55] Y. Li, T. Kunitake, S. Fujikawa, *Colloids Surf. A* **2006**, *275*, 209.

[56] R. Anselmann, H. Winkler, *Adv. Funct. Mater.* **2003**, *13*, 560.

[57] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.

[58] F. Li, S. A. Delo, A. Stein, *Angew. Chem.* **2007**, *119*, 6786; *Angew. Chem. Int. Ed.* **2007**, *46*, 6666.

[59] F. Schüth, F. Marlow, *Nature* **2007**, *449*, 550.

[60] A. van Blaaderen, R. Ruelt, P. Wiltzius, *Nature* **1997**, *385*, 321.

[61] L. V. Woodcock, *Nature* **1997**, *385*, 141.

[62] P. N. Pusey, W. van Megen, P. Bartlett, B. J. Ackerson, J. G. Rarity, S. M. Underwood, *Phys. Rev. Lett.* **1989**, *63*, 2753.

[63] O. Vickreva, O. Kalinina, E. Kumacheva, *Adv. Mater.* **2000**, *12*, 110.

[64] E. von Rhein, A. Bielawny, S. G. Weber, *Mater. Res. Soc. Symp. Proc.* **2006**, *901E*, 435.

[65] a) G. A. Ozin, S. M. Yang, *Adv. Funct. Mater.* **2001**, *11*, 95; b) P. Jiang, M. J. Mc Farland, *J. Am. Chem. Soc.* **2004**, *126*, 13778.

[66] Y. Xu, G.J Schneider, E. D. Wetzel, D. W. Prather, *J. Microlithogr. Microfabr. Microsyst.* **2004**, *3*, 168.

[67] a) L. K. Teh, N. K. Tan, C. C. Wong, and S. Li, *Appl. Phys. A* **2005**, *81*, 1399; b) A. Hartsuiker, W. L. Vos, *Langmuir* **2008**, *24*, 4670.

[68] S. L. Kuai, X. F. Hu, A. Hache, V. V. Truong, *J. Cryst. Growth* **2004**, *267*, 317.

[69] M. A. McLachlan, N. P. Johnson, R. M. De La Rue, D. W. McComb, *J. Mater. Chem.* **2004**, *14*, 144.

[70] Y. A. Vlasov, X. Z. Bo, J. C. Sturm, D. J. Norris, *Nature* **2001**, *414*, 289.

[71] S. Wong, V. Kitaev, G. A. Ozin, *J. Am. Chem. Soc.* **2003**, *125*, 15589.

[72] S. M. Yang, H. Miguez, G. A. Ozin, *Adv. Funct. Mater.* **2002**, *12*, 425.

[73] V. Kitaev, G. A. Ozin, *Adv. Mater.* **2003**, *15*, 75.

[74] J. Zhang, H. Liu, Z. Wang, and N. Ming, *J. Appl. Phys.* **2008**, *103*, 013517.

[75] J. Ye, R. Zentel, S. Arpiainen, J. Ahopelto, F. Jonsson, S. G. Romanov, C. M. S. Torres, *Langmuir* **2006**, *22*, 7378.

[76] Z. Zhou, X. S. Zhao, *Langmuir* **2004**, *20*, 1524.

[77] Y. Yin, Y. Lu, B. Gates Y. Xia, *J. Am. Chem. Soc.* **2001**, *123*, 8718.

[78] H. L. Li, F. Marlow, *Chem. Mater.* **2005**, *17*, 3809.

[79] H. L. Li, F. Marlow, *Chem. Mater.* **2006**, *18*, 1803.

[80] Y. K. Koh, C. C. Wong, *Langmuir* **2006**, *22*, 897.

[81] I. Popa, F. Marlow, *ChemPhysChem* **2008**, *9*, 1541.

[82] J. P. Hoogenboom, D. Derks, P. Vergeer, A. van Blaaderen, *J. Chem. Phys.* **2002**, *117*, 11320.

[83] M. Ishii, M. Harada, H. Nakamura, *Soft Matter* **2007**, *3*, 872.

[84] R. E. Beckham, M. A. Bevan, *J. Chem. Phys.* **2007**, *127*, 164708.

[85] W. G. Hoover, F. H. Ree, *J. Chem. Phys.* **1968**, *49*, 3609.

[86] D. J. Norris, E. G. Arlinghaus, L. Meng, R. Heiny, L. E. Schriven, *Adv. Mater.* **2004**, *16*, 1393.

[87] D. Gasperino, L. Meng, D. J. Norris, J. J. Derby, *J. Cryst. Growth* **2008**, *310*, 131.

[88] J. Townsand, *Opal. Extra-Lapis No. 10*, C. Weise, München, **1996**.

[89] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Ed.: S. Johnson), Wiley, New York, **2005**.

[90] Y. A. Vlasov, V. N. Astratov, A. V. Baryshev, A. A. Kaplyanskii, O. Z. Karimov, M. F. Limonov, *Phys. Rev. E* **2000**, *61*, 5784.

[91] The usual non-primitive fcc elementary cell consisting of 4 primitive unit cells of the fcc lattice. The value is a recalculation of the optimum values from reference [79], Figure 6, assuming the same probability of defects on the surface and in the volume. In the reference, the defect concentration is given in defects per number of spheres.

[92] A. S. Sinitskii, A. V. Knotko, Yu. D. Tretyakov, *Inorg. Mater.* **2005**, *41*, 1178.

[93] R. D. Pradhan, I. I. Tarhan, G. H. Watson, *Phys. Rev. B* **1996**, *54*, 13721.

[94] N. Tétreault, H. Míguez, S. M. Yang, V. Kitaev, G. A. Ozin, *Adv. Mater.* **2003**, *15*, 1167.

[95] P. Jiang, G. N. Ostojic, R. Narat, D. M. Mittleman, V. L. Colvin, *Adv. Mater.* **2001**, *13*, 389.

[96] Y. H. Ye, T. S. Mayer, I. C. Khoo, I. B. Divliansky, N. Abrams, T. E. Mallouk, *J. Mater. Chem.* **2002**, *12*, 3637.

[97] F. Jonsson, C. M. S. Torres, J. Seekamp, M. Schniedergers, A. Tiedemann, J. Ye, R. Zentel, *Microelectron. Eng.* **2005**, *78/79*, 429.

[98] Q. Yan, Z. Zhou, X. S. Zhao, S. J. Chua, *Adv. Mater.* **2005**, *17*, 1917.

[99] F. Fleischhaker, A. C. Arsenault, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. A. Ozin, *J. Am. Chem. Soc.* **2005**, *127*, 9318.

[100] S. A. Rinne, F. G. Santamaría, P. V. Braun, *Nat. Photonics* **2008**, *2*, 52.

[101] J. Li, P. R. Herman, V. Kitaev, S. Wong, G. A. Ozin, *Appl. Phys. Lett.* **2005**, *87*, 141106.

[102] W. Cai, R. Piestun, *Appl. Phys. Lett.* **2006**, *88*, 111112.

[103] R. Xie, T. Sekiguchi, D. Li, D. Yang, M. Jiang, *J. Phys. Chem. B* **2006**, *110*, 1107.

[104] L. A. Woldering, A. M. Otter, B. H. Husken, W. L. Vos, *Nanotechnology* **2006**, *17*, 5717.

[105] Y. Zhao, K. Wostyn, G. de Schaetzen, K. Clays, L. Hellemans, A. Persons, M. Szekeres, R. A. Schoonheydt, *Appl. Phys. Lett.* **2003**, *82*, 3764.

[106] M. Egen, R. Voss, B. Griesebock, R. Zentel, *Chem. Mater.* **2003**, *15*, 3786.

[107] P. Massé, S. Reculusa, K. Clays, S. Ravaine, *Chem. Phys. Lett.* **2006**, *422*, 251.

[108] a) N. Tetreault, A. Mihi, H. Miguez, I. Rodriguez, G. A. Ozin, F. Meseguer, V. Kitaev, *Adv. Mater.* **2004**, *16*, 346; b) N. Tetreault, H. Miguez, G. A. Ozin, *Adv. Mater.* **2004**, *16*, 1471.

[109] E. Palacios-Lidón, J. F. Galisteo-Lopez, B. H. Juarez, C. Lopez, *Adv. Mater.* **2004**, *16*, 341.

[110] N. Tétreault, A. Arsenault, A. Mihi, S. Wong, V. Kitaev, I. Manners, H. Miguez, G. A. Ozin, *Adv. Mater.* **2005**, *17*, 1912.

[111] F. Fleischhaker, A. C. Arsenault, Z. Wang, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. A. Ozin, *Adv. Mater.* **2005**, *17*, 2455.

[112] A. Stein, F. Li, N. R. Denny, *Chem. Mater.* **2008**, *20*, 649.

[113] Y. Cao, Y. Wang, Y. Zhu, H. Chen, Z. Li, J. Ding, Y. Chi, *Superlattices Microstruct.* **2006**, *40*, 155.

[114] H.-S. Kitzerow, A. Lorenz, H. Matthias in *Nanophotonic Materials: Photonic Crystals*, *Plasmonics*, *and Metamaterials* (Eds.: R. B. Wehrspورn, H.-S. Kitzerow, K. Busch), Wiley-VCH, Weinheim, **2008**, pp. 221–237.

[115] O. D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Nature* **1997**, *389*, 447.

[116] A. Imhof, D. J. Pine, *Nature* **1997**, *389*, 948.

[117] B. T. Holland, C. F. Blanford, A. Stein, *Science* **1998**, *281*, 538.

[118] A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, V. G. Ralchenko, *Science* **1998**, *282*, 897.

[119] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, H. M. van Driel, *Nature* **2000**, *405*, 437.

[120] Y. A. Vlasov, X. Z. Bo, J. C. Sturm, D. J. Norris, *Nature* **2001**, *414*, 289.

[121] F. Garcia-Santamaría, M. Ibisate, I. Rodriguez, F. Meseguer, C. Lopez, *Adv. Mater.* **2003**, *15*, 788.

[122] J. S. King, E. Graugnard, C. J. Summers, *Adv. Mater.* **2005**, *17*, 1010.

[123] M. Scharrer, X. Wu, A. Yamilov, H. Cao, And R. P. H. Chang, *Appl. Phys. Lett.* **2005**, *86*, 151113.

[124] Y. A. Vlasov, A. N. Yao, D. J. Norris, *Adv. Mater.* **1999**, *11*, 165.

[125] G. Subramanian, V. N. Manoharan, J. D. Thorne, D. J. Pine, *Adv. Mater.* **1999**, *11*, 1261.

[126] P. V. Braun, P. Wiltzius, *Nature* **1999**, *402*, 603.

[127] P. V. Braun, P. Wiltzius, *Adv. Mater.* **2001**, *13*, 482.

[128] A. Rugge, J. S. Becker, R. G. Gordon, S. H. Tolbert, *Nano Lett.* **2003**, *3*, 1293.

[129] Z. Lei, J. Li, Y. Zhang, S. Lu, *J. Mater. Chem.* **2000**, *10*, 2629.

[130] W. Dong, D. Bongard, B. Tesche, F. Marlow, *Adv. Mater.* **2002**, *14*, 1457.

[131] V. N. Astratov, V. N. Bogomolov, A. A. Kaplyanskii, A. V. Prokofiev, L. A. Samoilovich , S. M. Samoilovich, Y. A. Vlasov, *Nuovo Cimento* **1995**, *17*, 1349.

[132] F. Marlow, W. Dong, *ChemPhysChem* **2003**, *4*, 549.

[133] A. Blanco, C. Lopez, *Adv. Mater.* **2006**, *18*, 1593.

[134] W. Dong, H. J. Bongard, F. Marlow, *Chem. Mater.* **2003**, *15*, 568.

[135] W. Dong, F. Marlow, *Microporous Mesoporous Mater.* **2006**, *99*, 236.

[136] In fact, there are two German verbs possible: opaleszieren and opalisieren. These two can also have different meanings.

[137] R. Hanselmann, *RÖMPP*, Thieme Chemistry, RÖMPP online Version 3.2, **2008**. www.roempp.com.

[138] O. L. J. Pursiainen, J. J. Baumberg, H. Winkler, B. Viel, P. Spahn, T. Ruhl, *Opt. Express* **2007**, *15*, 9553.

[139] A. C. Arsenault, D. P. Puzzo, I. Manners, G. A. Ozin, *Nat. Photonics* **2007**, *1*, 468.

[140] A. C. Arsenault, D. P. Puzzo, A. Ghoussoub, I. Manners, G. A. Ozin, *J. Soc. Inf. Disp.* **2007**, *15*, 1095.

[141] S. H. Foulger, P. Jiang, A. Lattam, D. W. Smith, J. Ballato, D. E. Dausch, S. Greco, B. R. Stoner, *Adv. Mater.* **2003**, *15*, 685.

[142] A. C. Arsenault, H. Miguez, V. Kitaev, G. A. Ozin, I. Manners, *Adv. Mater.* **2003**, *15*, 503.

[143] A. C. Arsenault, T. J. Clark, G. von Freymann, L. Cademartiri, R. Sapienza, J. Bertolotti, E. Vekris, S. Wong, V. Kitaev, I. Manners, R. Z. Wang, S. John, D. Wiersma, G. A. Ozin, *Nat. Mater.* **2006**, *5*, 179.

[144] Y. Li, F. Cunin, J. R. Link, T. Gao, R. E. Betts, S. H. Reiver, V. Chin, S. N. Bhatia, M. J. Sailor, *Science* **2003**, *299*, 2045.

[145] D. Nakayama, Y. Takeoka, M. Watanabe, K. Kataoka, *Angew. Chem.* **2003**, *115*, 4329; *Angew. Chem. Int. Ed.* **2003**, *42*, 4197.

[146] J. Martorell, N. M. Lawandy, *Phys. Rev. Lett.* **1990**, *65*, 1877.

[147] S. V. Gaponenko, V. N. Bogomolov, E. P. Petrov, A. M. Kapitonov, D. A. Yarotsky, I. I. Kalosha, A. A. Eychmueller, A. L. Rogach, J. McGilp, U. Woggon, F. Gindele, *J. Lightwave Technol.* **1999**, *17*, 2128.

[148] K. Nozaki, S. Kita, T. Baba, *Opt. Express* **2007**, *15*, 7506.

[149] M. Scharrer, A. Yamilov, X. Wu, H. Cao, R. P. H. Chang, *Appl. Phys. Lett.* **2006**, *88*, 201103.

[150] K. Sakoda, *Optical Properties of Photonic Crystals*, Springer, Berlin, **2001**, chap. 5.

[151] M. Notomi, K. Yamada, A. Shinya, J. Takahashi, C. Takahashi, I. Yokohama, *Phys. Rev. Lett.* **2001**, *87*, 253902.

[152] H. Gersen, T. J. Karle, R. J. P. Engelen, W. Bogaerts, J. P. Korterik, N. F. van Hulst, T. F. Krauss, L. Kuipers, *Phys. Rev. Lett.* **2005**, *94*, 073903.

[153] Yu. A. Vlasov, M. O'Boyle, H. F. Hamann, S. J. McNab, *Nature* **2005**, *438*, 65.

[154] M. Soljacic, J. D. Joannopoulos, *Nat. Mater.* **2004**, *3*, 211.

[155] See e.g.: H. J. Eichler in Bergmann-Schaefer, *Lehrbuch der Experimentalphysik*, *Vol. 3*, 8th ed., Walter de Gruyter, Berlin, New York, **1987**, p. 216.

[156] See e.g.: A. Figotin, I. Vitebskiy, *Waves in Random and Complex Media* **2006**, *16*, 293.

[157] S. Nishimura, N. Abrams, B. A. Lewis, L. I. Halaoui, T. E. Mallouk, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, *J. Am. Chem. Soc.* **2003**, *125*, 6306.

[158] J. I. L. Chen, G. von Freymann, S. Y. Choi, V. Kitaev, G. A. Ozin, *Adv. Mater.* **2006**, *18*, 1915.

[159] G. von Freymann, S. John, S. Wong, V. Kitaev, G. A. Ozin, *Appl. Phys. Lett.* **2005**, *86*, 053108.

[160] G. von Freymann, V. Kitaev, G. A. Ozin, *J. Am. Chem. Soc.* **2007**, *129*, 1196.