Self Assembly of Low-Emissivity Materials (SALEM)

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Self-assembly techniques employing liquid emulsions and colloidal suspensions for the fabrication of photonic crystals are described. To make the photonic crystals, monodisperse emulsion droplets or solid colloidal particles are first allowed to self-assemble into close-packed crystals, having predominately face-centered cubic (fcc) order. Second, the interstices are filled with a high-refractive-index material, usually titania, using either sol-gel chemistry or by compacting nanoparticles. Finally, the templating emulsion droplets or colloidal particles are removed leaving behind a porous solid in which the spherical pores are ordered on a crystalline lattice (fcc). The primary advantages of emulsion templating of photonic crystals is that large monoliths up to 10 mm in size can be produced and that they can be made in the high-refractive-index rutile phase of titania. The primary advantage of the colloidal templating technique is that more perfect crystalline structures can be made, though the overall sample size is generally only about a millimeter or smaller in size and the lower-refractive-index anatase phase of titania is usually produced. In addition, highly scattering porous titania spheres, about 5 microns in diameter, can be made using a combination of colloidal and emulsion templating techniques. These may be useful as pigments in paints.
Final Progress Report
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(SALEM)

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1 Statement of problem studied

The aim of this grant was to develop self-assembly techniques to fabricate photonic crystals which could be useful for controlling emissivity, improving laser efficiency, and for other optical applications. Prior to the commencement of this grant, all methods for producing photonic crystals were based on the micro-lithography techniques using in the semi-conductor industry or on direct machining. As such techniques were not capable of producing the 3-dimensional periodic structures at the sub-micron length scales required to produce photonic crystals in the visible and near infrared, we proposed using colloidal and emulsion self-assembly to develop methods which could produce photonic structures at the requisite sub-micron length scales.

2 Summary of important results

2.1 Introduction

The single most important outcome of this research program was the development of self-assembly techniques for the fabrication of photonic crystals. Our original paper (Manuscript 2), published at the outset of this program, was the first paper on this topic in the scientific literature, and has lead to a plethora of subsequent papers published by dozens of research groups throughout the world (Manuscript 2 has been cited over 90 times since its publication). These techniques currently represent the most promising path towards the creation of photonic crystals with full 3-dimensional optical bandgaps (i.e. at optical frequencies).

In the course of this short two-year program, we developed both emulsion and colloidal templating techniques for making photonic crystals. The two techniques have different strengths and weaknesses. The choice of technique depends on the type of material to be used as well as on various design constraints, which are summarized in greater detail later in this report.

We also made a number of different types of photonic crystals using a variety of materials. Some materials, such as titania or silica, are suitable for applications at visible wavelengths, while other materials used, such as silicon, are suitable for use at infrared wavelengths.

We also developed a new kind of colloidal particle, which is an extremely highly efficient scatterer of light, and which may find application as a paint pigment. These particles are on the order of one to several microns in diameter, are usually made of some high refractive index material such as titania, and contain a close packing of holes whose diameters are comparable to the wavelength of light (i.e. a few hundred nanometers). We call these particles "supraballs" and describe them in greater detail in Section 2.3.

On the theoretical front, we studied the effects of disorder in photonic crystals. We also numerically examined the bistable properties of nonlinear photonic crystals. The in and out
of plane propagation of EM waves in 2d photonic crystals was examined.

Our calculations indicated that the gaps in photonic crystals are robust and can sustain a large amount of disorder. This is similar to the case of amorphous semiconductors where the gap is due to short range order and not to long range order. The time-dependent switching properties of nonlinear photonic crystals were examined. It was found that the response of the system is characterized by both stable and self-pulsing solutions. In and out of plane propagation of EM waves was studied numerically for 2d systems and found to be in excellent agreement with experiments.

2.2 Photonic crystals by self-assembly methods

Photonic crystals are materials with a periodic modulation of the refractive index (or dielectric constant) and with little or no absorption of light.\(^9\) The modulation of the refractive index leads to "stop bands" where light does not propagate over a range or "band" of frequencies in certain directions with respect to the photonic crystalline axes. Theory shows that if the certain conditions are met, the stop band can extend in all directions over a finite range of frequencies.\(^{10,11}\) In such a case, the photonic crystal is said to have a full (or omnidirectional) photonic band gap. In this report, we shall refer to full omnidirectional photonic bandgaps simply as "photonic bandgaps" or "PBGs." Any other absence of propagating modes for a certain frequency band but only over a finite range of directions shall be referred to as a "stop band."

In this project, we focused on developing methods for making a photonic crystal consisting of face-centered cubic (fcc) periodically spaced holes in a high-dielectric solid matrix. This structure was chosen for several reasons: (1) such a material is predicted by theory to have a 3-d bandgap between the eighth and ninth bands when the refractive index of the solid matrix is greater than 2.85;\(^{10,11}\) (2) monodisperse microspheres spontaneously self-assemble into a close-packed fcc structure (albeit sometimes with stacking faults);\(^{12}\) (3) monodisperse spheres can be fabricated from various polymers, from silica, as well as from various liquids, and then suspended in some (other) suitable liquid; they can then used as templates around which high-index material such as titania can be grown or assembled.

The primary reasons for choosing a self-assembly approach to making photonic crystals is that the technique is relatively inexpensive and because other techniques, such as those used in the microelectronics industry, are ill-suited for making large 3-dimensional structures, especially with dielectric modulations at the small length scales (0.2-1.0 \(\mu m\)) needed for making PBGs at optical and near-infrared wavelengths. In the next two sections we describe emulsion templating and colloidal templating, providing examples of each, and describing the relative merits and drawbacks of each.
2.2.1 Emulsion templating

Emulsion templating was first described in a paper we published a few months after the beginning of the funding period (Manuscript 2). Since that first publication, the procedure has been improved in numerous ways. Perhaps the most important improvement is in the development of a method for producing extremely monodisperse emulsion droplets which self-assemble into fcc lattices and can then be used as templates for growing photonic crystals. This method consists of the swelling of monodisperse polymer spheres with a liquid which dissolves the spheres and is described in Manuscript 9. The resulting monodisperse emulsion is stabilized with a triblock copolymer surfactant and added to a alkoxide sol suspended in formamide. The emulsion is concentrated by centrifugation causing the emulsion droplets do crystallize in a fcc lattice. The sol is then polymerized to produce a titania network. Removal of the emulsion template and other liquids by solvent extraction and subsequent drying produces a monolithic solid photonic crystal consisting of holes left by the emulsion template. X-ray diffraction shows that prior to calcination, the titania made from an emulsion template is mostly amorphous.\textsuperscript{13} After calcination, most of the titania is converted to the rutile phase with the degree of conversion depending primarily on the temperature at which the sample is heated. Photonic crystals prepared in this way is shown in Fig. 1. While not immediately appreciated, the fact that the emulsion templating technique produces titania that is converted to the high-refractive-index rutile phase is significant. It looms even more important with the realization that all other proven self-assembly techniques for fabricating photonic crystals (e.g. colloidal templating) produce titania in the
Figure 2: Porous photonic crystals made using colloidal templating. (a) Silica. (a) Titania (anatase). Expanded view in inset shows individual titania grains. The white scale bars are 1 \( \mu \text{m} \) in length.

low-refractive-index \textit{anatase} phase.\textsuperscript{2,3} It is only the high-refractive-index rutile phase of titania which has a sufficiently high refractive index (\( > 2.85 \)) to produce an fcc photonic crystal with a full photonic bandgap.

One advantage of the emulsion templating technique is that the templating spheres can be removed at room temperature leaving behind a porous photonic crystal. This avoids the differential shrinkage and cracking associated with heating during the removal of polymer-particle templates in many other colloidal templating techniques.\textsuperscript{2,3} As a consequence, much larger photonic crystals can be achieved (as large as 10 mm \( \times \) 10 mm \( \times \) 5 mm). After removal of the emulsion template, the sample can be safely heated without significant cracking. There is some growth of the titania grains, however, as can be seen from the larger titania grain sizes in Fig. 1(b) than in Fig. 1(a).

2.2.2 Colloidal templating

Colloidal templating is an alternative to emulsion templating which offers many advantages and some disadvantages. The basic technique we developed is described in Manuscript 7. In this technique, small titania particles with diameters on the order of 30 nm are mixed with a suspension of highly monodisperse microspheres made from polystyrene, silica, or some other suitable material. Drying the suspension causes the small titania particles to concentrate and sinter together in the interstices between the densely packed microspheres. The microspheres are then removed by heating or other means leaving behind a highly order photonic crystal as shown in Fig. 2.

In contrast to methods which use sol-gel chemistry to produce the titania matrix, the colloidal templating method we developed results in minimal shrinkage (\( < 6\% \)). Consequently,
there is little cracking. The typical size of samples produced by this method is approximately 3 mm × 2 mm × 1 mm.

The primary advantage of our colloidal templating technique is that it produces nearly perfectly ordered photonic crystals as can be seen from 2. These typical grain sizes of a photonic crystallite within these photonic crystal are 10 μm to 50 μm. The primary drawback of photonic crystals made in this way is that high-quality crystals currently can only be fabricated in the anatase phase. This is because colloidal titania with particle sizes in the requisite 10 nm to 30 nm size range are currently available only in the low-index anatase phase.

2.2.3 Infrared materials

Another advantage of the colloidal templating technique is that it is extremely versatile; it can be used to make photonic crystals from virtually any material that can be produced as a powder. We demonstrated this by making the first photonic crystals from silicon, a material with low absorption and high dielectric constant in the near infrared (Manuscript 18). The results shown in Fig. 3 illustrate that the method produces photonic crystals of excellent quality. In contrast to the silica and titania photonic crystals made by the colloidal templating technique, the silicon photonic crystals are very fragile. The is consistent with poor sintering between the silicon particles from which the sample was made.
2.3 Photonic paint: "Supraballs"

One goal of the HIDE program was to develop low-emissivity coatings which could be applied to a variety of materials. To further progress towards this goal, we developed a new kind of structured titania particle, which we call a "supraball." These supraballs show great promise for being used as the essential component in a paint. If successful, the paint could be applied to a wide variety of surfaces and impart the advantageous properties of photonic crystals to that surface: very strong scattering of radiation and low emissivity.

Two scanning electron micrographs of supraballs made in our lab are shown in Fig. 4. As can be seen from the figure, the supraballs are porous titania spheres. The pores are close-packed and range in size from about 10% to 25% of the size of the titania particle itself. By tuning the pores to be of an appropriate size (comparable to the wavelength of light), the particles can be made to be highly scattering. It might even be possible to achieve a photonic band gap within the particle if the pores within the particle are ordered and there are one the order of 5 or more photonic crystal unit cells. While the technique for making such particles is still under development, we believe these particles to represent one of the more promising routes to practical photonic materials.

2.4 Shells and monodisperse emulsions

A wide variety of structures can be made with emulsion templates. One such structure, described in Manuscript 6 consists of titania shells which may be structured, if so desired, in the form of a titania foam. In Fig. 5, we show scanning electron micrographs of titania shells and a titania foam made by this technique.
Figure 5: (a) Titania (rutile) shells and (b) a foam made by emulsion templating. The white scale bars are 10 μm in length.

2.5 Hierarchically-ordered photonic materials

Because of the versatility of the emulsion and colloidal templating techniques, they can be combined with other micro-fabrication methods to make an incredible variety of structured materials. In particular, these techniques can be combined with methods for making both larger and smaller structures. The result can be a material with a hierarchy of structures over a wide range of length scales. To demonstrate this capability, we combined colloidal templating with micro-contact printing and templating of mesoporous materials using lyotropic liquid crystalline mesophases. With micro-contact printing, we can make materials length scales of tens of microns. Using lyotropic liquid crystal templates, we can produce structures on length scales on the order of ten nanometers. These two length scales conveniently lie on either side of the length scales we can access with colloidal templating techniques. Our results are summarized in Manuscript 5.

In Fig. 6, we show one of the results of our attempts to make hierarchically-structured materials. In fact, our results demonstrate not only that it is possible to create such structures, but that it is also possible to simultaneous order the structures on all three different length scales. Figures 6(a)-(b) show a pattern of hexagons connected by long arms that was created by the micro-contact printing method. Figures 6(b)-(d) show the macropores created by the colloidal templating technique. Note that the ordering in the hexagonal pads triangular or hexagonal while that in the arms is square or cubic. This reflects the influence of the walls of the stamp used in the micro-contact printing process. Finally, Figs. 6(e)-(f) show the mesoporous structure created by the liquid crystal template in the walls shown in Figs. 6(b)-(d). The walls show ordered mesoporous structures with lattice spacings on the order of 10 nm. These remarkable hierarchically-ordered structures demonstrate the power of these templating techniques.
2.6 Conclusion

Over the brief period of time this project was funded, we developed and demonstrated a number of new methods for making new and exciting photonic materials using self-assembly techniques. Since that time, the number of scientists and engineers developing self-assembly methods for fabricating photonic crystals has exploded. While development of these methods is still in its infancy, self-assembly methods already represent the most successful approach for making photonic crystals with significant stop bands in the visible and near infrared. Development of these techniques is expected to proceed rapidly. Perhaps the greatest limitation at this time is that only close-packed structures can currently be made using colloidal or emulsion templating methods. Unfortunately, the requirements to produce photonic bandgaps from close-packed structures put severe demands on the materials, self-assembly, and processing. While it is difficult to predict where a new technology may go, one promising approach may be to develop self-assembly methods for producing structures other than close-packed crystals. Among these, the diamond and related structures have the most attractive photonic properties. Producing such structures with self-assembly techniques represents one of the most promising avenues for future research.
3 Publications & technical reports

3.1 Papers published in peer-reviewed journals


3.2 Papers published in conference proceedings


3.3 Papers submitted but not yet published


3.4 Papers presented at meetings


"Localization of Classical Waves and Photonic Band Gaps,” C. M. Soukoulis, University of Amsterdam, Netherlands, April 1999


4 Scientific personnel supported by this project

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5 Report of Inventions

Method for the production of porous ceramics.

6 Bibliography

References