Photonic Crystals from Emulsion Templates**

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1. Introduction

The emergence of the field of photonic crystals has led to a surge of research on the fabrication of macroporous materials. Calculations show that a complete optical photonic bandgap may be observed if such materials have a sufficiently high index of refraction and contain ordered pores with periodicity on the order of the wavelength of visible light.[1] With a complete gap there is a range of frequencies for which electromagnetic waves cannot propagate through the material. This property leads to a plethora of possible applications in optical devices.[2]

The challenge of producing a three-dimensionally ordered material with lattice constants on the order of micrometers or below has led several groups to monodisperse colloids, which are easily produced at the requisite length scales and self-assemble into the face-centered-cubic (fcc) crystal structure under certain conditions. Such “artificial opals”, as they are known, can be infiltrated with a second material and transformed to an ordered macroporous material, or air-sphere crystal, after the removal of the opal template. The resulting “inverse opal” structure has certain optical advantages over the original template.[1]

Commonly used opal templates include colloidal crystals of silica spheres,[3,4] which can be removed by dissolution in hydrofluoric acid, or polystyrene spheres,[5,6] which can be removed by calcination. In photonic crystals designed for the visible region of the spectrum the infiltrated phase is typically titanium dioxide (titania), introduced as either a liquid sol or a particulate suspension.[7,8] For an fcc lattice of pores the index of refraction of the solid phase must be approximately 2.9 for the material to have a complete bandgap.[1,9] Titania is one of the few non-absorbing dielectrics suitable for visible wavelengths; however, only one crystalline phase—the rutile phase—has such a high index. Unfortunately there are processing difficulties with retaining the pore structure of the material while converting the matrix phase to the equilibrium rutile phase from the kinetically favored (but lower index) anatase phase.

Here we discuss a fabrication scheme, emulsion templating, that employs monodisperse liquid droplets instead of solid particles as the colloidal template[10] and that can be used to produce porous rutile titanium dioxide. We discuss the advantages and disadvantages of the approach, the properties of the materials we have produced, and the prospects for building photonic bandgap materials by emulsion templating. Although the method may be used to produce a variety of inorganic and organic porous materials,[11] we discuss only the preparation of porous titania.

2. Emulsion Templated Materials

The basic scheme for the emulsion templating approach is as follows: we prepare a monodisperse emulsion—a uniform suspension of liquid oil droplets stabilized by surfactant and suspended in a second, immiscible liquid—in a titania sol. The sol is a solution of titanium dioxide oligomers in the polar liquid formamide. Sedimentation or centrifugation increases the
volume fraction of oil droplets until they are close packed and ordered. After the formation of this emulsion colloidal crystal, a catalyst is added to gel the sol, or crosslink the oligomeric species. Once a gel has formed, the liquid droplets may be easily removed by immersing the entire structure in a solvent (ethanol, for example) that can permeate the gel and dissolve the oil. After removal of the template the gel is aged, dried in air, and calcined to transform the matrix to the rutile phase.

The primary difference between this approach and other colloidal crystal templating methods is that the emulsion colloidal crystal consists of deformable, easily dissolved particles. The deformability allows the material to withstand the stresses of shrinkage during gelation without cracking; similarly the removal of the template (by dissolving the droplets) before drying and firing prevents fracture and obviates the need for multiple infiltrations of titania sol.[6] We note that although the method avoids stresses associated with constrained shrinkage of the gel, there are still stresses due to capillary forces during drying that limit the ultimate size of the sample.[12]

A second advantage is that the method easily yields the rutile titania phase with grain sizes sufficiently small so as not to destroy the pore structure. To our knowledge this is the only titania templating method that yields the high index of refraction rutile phase rather than the low index anatase phase. Powder X-ray diffraction reveals that the transformation from anatase to rutile is complete at 1000 °C and that the rutile grain size is approximately 70 nm. Nitrogen adsorption measurements indicate that the rutile matrix phase is nearly completely dense after calcination. Thus we expect that the effective index of refraction of the matrix should be close to that of the bulk value for rutile. We do not yet understand why this method is able to produce porous rutile while other templating methods fail; however, since the anatase-to-rutile phase transition is a non-equilibrium one, the transition temperature is highly dependent on the synthesis conditions,[13–15] so it is reasonable to conclude that the final grain size is also dependent on the fabrication procedure.

The principal disadvantages of the method are the effort involved in producing monodisperse emulsions and the small domain sizes of the crystals formed by the droplets. Figure 1 shows an emulsion sample prepared by fractionating a crude, polydisperse emulsion. Although quite monodisperse by emulsion standards, the sample is not as monodisperse as polystyrene or silica microsphere standards, which typically have polydispersities of 5 % or lower, as determined by the relative standard deviation in the particle diameter distribution. Nonetheless with great effort it is possible to produce emulsions with polydispersities as low as 10 % using the fractionation technique; Figure 2a shows the scanning electron micrograph of a rutile sample with 200 nm pores made by templating such an emulsion. The bulk sample, a pellet 1 cm in diameter and 1 mm thick, can be seen in the inset.

Fig. 1. Optical micrograph (Nomarski method) of monodisperse (15 % polydispersity) oil in water emulsion. Inset shows 2.5× magnified view of an ordered region.

One way to reduce the amount of fractionation required to achieve a given polydispersity is to start with a quasi-monodisperse emulsion prior to fractionating. It is possible to produce droplets with nearly 30 % polydispersity with a shearing method developed by Mason and Bibette.[17] A sample produced by templating a sheared emulsion subjected to a small number of fractionation steps is shown in Figure 2b.

A second approach is to use a suspension of polymer microspheres where the polymer has a low glass transition temperature. Emulsion polymerization may be used to prepare such particles with uniformity comparable to polystyrene microsphere standards. Above the glass transition temperature, a polymer particle has similar properties to the liquid emulsion droplet: it is deformable and can be easily dissolved prior to drying the gel. A porous rutile structure produced from a template of ordered poly(butyl methacrylate) spheres (glass transition near room temperature) is shown in Figure 2c.

For the sample in Figure 2a we have measured the transmitted intensity of normally incident light as a function of wavelength. The spectrum, shown in Figure 3, can be compared to the spectrum for a non-porous sample and to a sample with disordered pores of approximately the same diameter. Each sample was prepared in the same manner except for the emulsion used: no emulsion was used in preparing the non-porous sample, and a polydisperse emulsion was used in preparing the sample with disordered pores. The data indicate that the ordering of the 200 nm pores leads to a wide minimum centered near 500 nm.

3. Prospects and Conclusions

The emulsion templating method yields ordered macroporous titania with high index contrast. Though the ordering of the droplets in the colloidal crystallites is sufficiently good for the samples to exhibit minima in the transmission spectrum, it is not yet clear whether the lattice of pores can be made uniform enough for the material to exhibit a bandgap. We can improve the ordering by using a more monodisperse suspen-
sion such as a sheared and fractionated emulsion or a low
glass transition emulsion polymer. Unfortunately, recent cal-
culations\[19,20\] have shown that the bandgap of an inverse opal
with a refractive index of 2.9—the minimum index necessary
to open a full bandgap and the highest index of rutile titania
below its absorption frequency—is extremely sensitive to dis-
order. Even the positional disorder arising from the small
polydispersity in a polystyrene latex template may be suffi-
cient to close the bandgap. Although Blanco et al. have shown
evidence of a bandgap at near-infrared wavelengths in a sili-
con inverse opal,\[21\] the refractive index of silicon in the infra-
red (3.45) allows the bandgap to persist at higher amounts of
disorder than would be possible at visible wavelengths, where
few materials are known to have purely real indices above 3.0.

There is a second source of disorder in these materials
besides the defects in the pore lattice. There is likely strong
scattering within the dielectric phase due to the large (nearly
100 nm), randomly oriented rutile crystallites. Very little is
known about the effects of disorder within the matrix phase
of an inverse opal photonic crystal, but given the sensitivity of
the inverse opal bandgap to lattice disorder, one would expect
that the gap is also sensitive to this second type of disorder. It
would therefore appear that the prospects for making photon-
ic crystals with bandgap in the visible from inverse opals of

Fig. 2. Scanning electron micrographs of porous rutile titania. a) Prepared
from fractionated emulsion. Inset shows photograph of bulk sample.
b) Prepared from emulsion produced by shearing technique of Mason and
Bibette and subsequently fractionated. c) Prepared from low glass transi-
tion temperature poly(butyl methacrylate) microspheres.

Fig. 3. Optical transmission intensities, scaled by unscattered intensity $I_0$, versus
wavelength for a non-porous titania sample (top), a sample with disordered
250 nm diameter pores (middle), and a sample with ordered 200 nm pores (bot-
tom). All samples were subjected to the same emulsion templating processing steps.
rutile titania, and indeed from any inverse fcc opal, are dim. A diamond lattice of pores, which has a large, robust gap at lower refractive index contrast\[^{[22]}\] is far preferable to the fcc structure, but there are no known ways to make colloidal crystals with diamond symmetry. However, inverse opals may yet find uses in optical devices due to their broad stop bands or perhaps even in paints due to their strong scattering and low density. For these applications the emulsion templating scheme has the distinct advantage of being able to produce large volumes of sample from inexpensive precursors such as oil and surfactant.

Finally we note that there are many approaches to preparing three-dimensional photonic crystals in the visible other than those involving inverse opals. Among the most promising candidates are holographic, lithography,\[^{[23]}\] and microfabrication.\[^{[24]}\] In addition, the macroporous materials produced by colloidal crystal templating have many other applications in catalysis and separations.

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