# Ordered macroporous rutile titanium dioxide by emulsion templating

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## ABSTRACT

We discuss a method for fabricating photonic crystals of closely packed air spheres with diameters on the order of 300 nm in a rutile titania matrix. These differ from the air sphere/titania materials reported elsewhere in that the matrix is the high-index rutile phase of titania ($n \approx 2.9$) as opposed to the low-index anatase phase ($n \approx 2.4$). We make these materials by a sol-gel process with oil-in-formamide emulsions as templates. The emulsion droplets are stable and have a polydispersity of 15% or less, allowing them to form small colloidal crystallites when concentrated in a titania sol. The oil template can be removed after gelation of the sol and prior to drying, allowing us to produce monolithic samples with few cracks. Calcination at 1000 °C converts the structure to the rutile phase with an average crystallite size of 60 nm. Optical transmission spectra show the presence of a broad minimum at a wavelength of 500 nm for a sample with ordered 200 nm pores.

**Keywords:** Photonic crystal, macroporous, titania, rutile, emulsion templating, sol gel

## 1. INTRODUCTION

Photonic crystals, periodic arrangements of dielectric materials, have garnered much attention recently due to their possible applications in waveguides, lasers, and other telecommunications and optical devices.[1] Under certain conditions it is possible for a crystal to exhibit a photonic band gap (PBG), a region of frequencies for which electromagnetic waves cannot propagate through the material. For a crystal made from two dielectrics materials to display a PBG, the refractive index contrast, defined as the ratio of the higher index ($n_2$) to the lower index ($n_1$), must be sufficiently high while the absorption of the two materials must be sufficiently low. The critical contrast required to achieve a PBG depends on the arrangement of the dielectrics.

Typically the wavelength at the center of the band gap is on the order of the lattice spacing in the crystal. Since our goal is to achieve a band gap at optical wavelengths (approximately 0.5 $\mu$m), we have chosen to employ monodisperse spherical colloidal particles in our fabrication scheme. Such particles will undergo a spontaneous transition to a crystalline phase at a certain volume fraction in the absence of strong attractions between particles. The resulting crystals typically have lattice spacings on the order of 0.5 $\mu$m and exhibit Bragg diffraction for visible wavelengths.[2]

Recent theoretical work[3,4] has shown that PBG materials can be fabricated from a face-centered cubic (FCC) lattice of closely packed air spheres (or pores, with $n_1 = 1$) in a high dielectric ($n_2 \approx 3$) matrix. One strategy to prepare such a structure is to use a colloidal crystal as a template for a sol-gel process that occurs in the interstices of the crystal.[5] The air sphere structure is formed after removal of the template and densification of the gel.

The rutile phase of titanium dioxide ($TiO_2$, or titania) is one of the only materials available with a sufficiently high refractive index ($n \approx 2.9$) and sufficiently low absorption to allow fabrication of a photonic crystal with a band gap at optical wavelengths. Although several groups[6–8] have reported the successful fabrication of air sphere/titania photonic crystals using colloidal crystals of polystyrene spheres as templates in a sol-gel process, their procedures result in the anatase phase of titania, which has a significantly lower refractive index ($n \approx 2.4$) than rutile. Attempts to convert the structure to rutile by heat treatment have been unsuccessful; generally the pore structure is destroyed by excessive grain growth of titania.

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Here we discuss a method of fabricating air sphere/titania photonic crystals by a process called emulsion templating. We start by giving an overview of the general procedure, then show how the technique leads to the desired microstructure. Our approach differs from those of other groups using colloidal crystals as templates in that we use monodisperse emulsion droplets (liquid colloidal particles) instead of polystyrene spheres. This approach has two main advantages. The first is that the emulsion droplet template can be removed prior to further processing of the gel. Since considerable shrinkage of the high dielectric matrix can occur during drying and heat treatment, removal of the template allows us to produce monolithic samples with few cracks. The polystyrene sphere templates, on the other hand, are removed during heat treatment; usually (with the exception of the method in Ref. 8) the shrinkage which occurs prior to heating results in a powdery sample. The second advantage of our approach is that we can easily obtain the rutile phase while retaining the pore structure of the material.

The primary disadvantage of the emulsion templating technique is the difficulty in obtaining emulsions with sufficient monodispersity to crystallize. Monodisperse polystyrene spheres, on the other hand, are readily prepared by chemical means.[9]

## 2. EXPERIMENTAL DETAILS

### 2.1. Preparation of Monodisperse Emulsions

We first prepare a polydisperse oil-in-water emulsion by mixing 15% v/v isooctane (the oil) with a solution of sodium dodecyl sulfate (SDS, a surfactant) in water by hand. The mixture is then sheared in a homogenizer at several thousand rpm in order to break up the emulsion into droplets with diameters from $0.1\,\mu$m to $3\,\mu$m. This polydisperse emulsion is then fractionated[10] several times until the polydispersity of the fractions becomes small enough that the emulsion appears iridescent when viewed as a thin layer between glass plates.

To reduce the amount of fractionation steps required to achieve a small polydispersity we can prepare the initial emulsion by the shearing technique of Mason and Bibette.[11] For this procedure typically we mix 70% v/v silicone oil with a concentrated solution of the nonionic surfactant Igepal C0-610 in water. The emulsion is then sheared in a Couette geometry with a small gap ($<200\,\mu$m) at a rate of approximately $1000\,\mathrm{s}^{-1}$, resulting in an emulsion with ~30% polydispersity (standard deviation in the diameter), as measured by static light scattering. Subsequent fractionation results in an emulsion with ~15% polydispersity, which is small enough that the emulsion shows some regions where the droplets are ordered in a triangular lattice (Fig. 1).

### 2.2. Sol-gel Technique and Nonaqueous Emulsions

Titania sols are prepared from titanium isopropoxide and acetylacetone (chelating agent) according to the method in Ref. 5. The sol is simply a mixture of short polymers (oligomers) of titanium oxide dissolved in a polar solvent. Because titanium alkoxides are highly reactive with water and precipitate immediately upon exposure it is necessary to use a different solvent for the titania precursor. The choice of solvents is limited since the emulsion must remain colloidally stable when transferred to the titania sol. We have found[12] that emulsion stability can be maintained if the polar liquid formamide, instead of water, is used as the continuous phase, along with certain types of triblock copolymers as surfactants. Since formamide is not reactive with titanium alkoxides, it is an ideal choice for the sol.

### 2.3. Templating Procedure

A pictorial overview of the emulsion templating procedure is shown in Fig. 2. First, our monodisperse emulsion (prepared and fractionated in water) is transferred to the formamide-titania sol. Centrifugation is used to concentrate the emulsion to a volume fraction of 50% or more, so that ordering can occur. The sol is then gelled by the addition of ammonium hydroxide; during this step the oligomers in the sol react with each other to form a loosely cross-linked network in the spaces between the emulsion droplets.

The critical step in the process now follows. The gel is submerged in alcohol or another liquid that dissolves the oil in the droplets. After a few such rinses the material consists of an ordered array of pores filled with alcohol in a semi-solid gel swollen with alcohol. We then slowly evaporate the alcohol from the pores and the gel. During this stage the entire structure shrinks, but stresses and cracking are minimized because the densification of the gel is not constrained by the presence of an incompressible template. Calcination at 1000 °C for two hours results in a microstructure comprising air spheres in a rutile matrix.

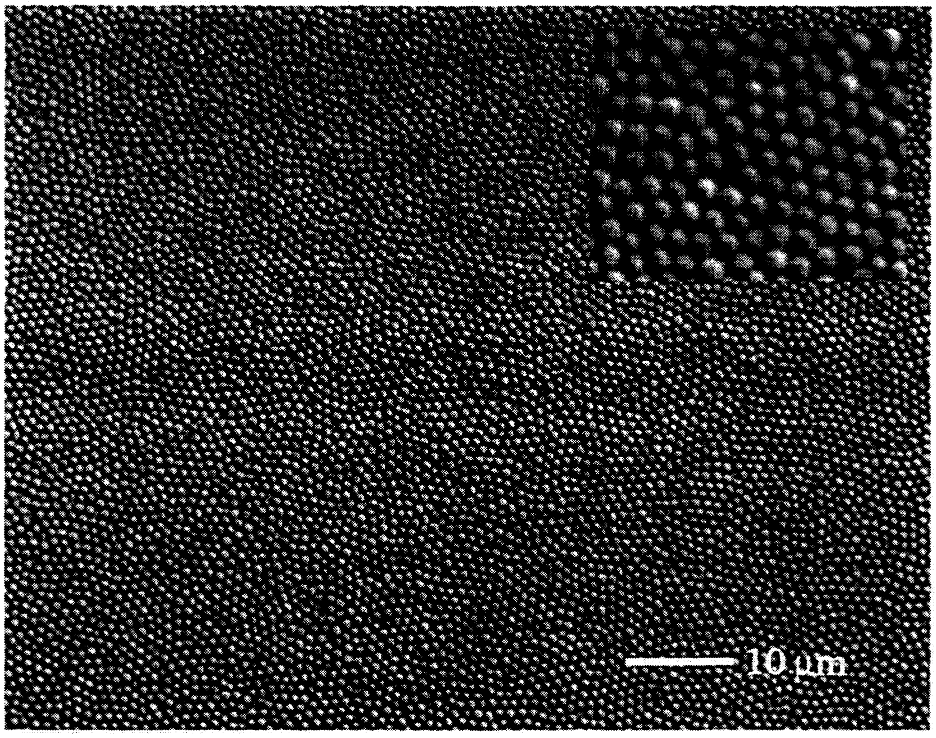

**Figure 1.** Optical micrograph (Nomarski method) of monodisperse (~15% polydispersity) silicone oil-in-water emulsion prepared by shearing and fractionation. Inset shows 2.5X magnified view of an ordered region. Droplets are approximately 1 $\mu$m in diameter.

### 2.4. Analyses

The microstructure of the samples was characterized in a JEOL 6300F field emission scanning electron microscope (SEM). To prepare samples for SEM we broke small pieces off of our materials to reveal the internal pore structure and then sputter coated them with gold.

Crystalline phases were determined by powder X-ray diffraction in a Philips X'pert-MPD diffractometer using Cu-K$\alpha$ radiation. Samples were ground by hand to a fine powder.

To probe the band structure of the samples we measured the optical transmission as a function of wavelength. A xenon arc lamp is the source for a monochromator (band width 2 nm) that provides the incident light. The transmitted intensity was measured with a photodiode.

## 3. RESULTS AND DISCUSSION

Figure 3 shows a macroporous rutile titania sample prepared from an emulsion with average droplet diameter 1 $\mu$m. In some regions the pores are arranged in a triangular lattice. The pores do not appear to be closely packed (*i.e.*, they are not touching) because they are "decapitated" by the surface; further SEM analysis (not shown) shows that below the surface the pores have diameter 200 $\mu$m, which matches the inter-pore spacing shown in Fig. 3. The bulk sample is a cylindrical monolith measuring 1 cm in diameter by 1 mm thick.

We used powder X-ray diffraction to characterize the phase of samples heated to a given temperature for two hours (Fig. 4). The anatase phase, with its characteristic [101] reflection at $2\theta = 25°$, is the only crystalline phase seen at temperatures less than 800 °C. Above this temperature diffraction maxima corresponding to the rutile phase start to appear; at 1000 °C the transformation to rutile is complete. The average anatase crystallite size at 400 °C is 7 nm, as estimated by the Scherrer equation, and gradually increases as temperature increases. At 1000 °C the average rutile grain size is 60 nm. The size of the rutile grains is not insignificant compared to the size of the pores in

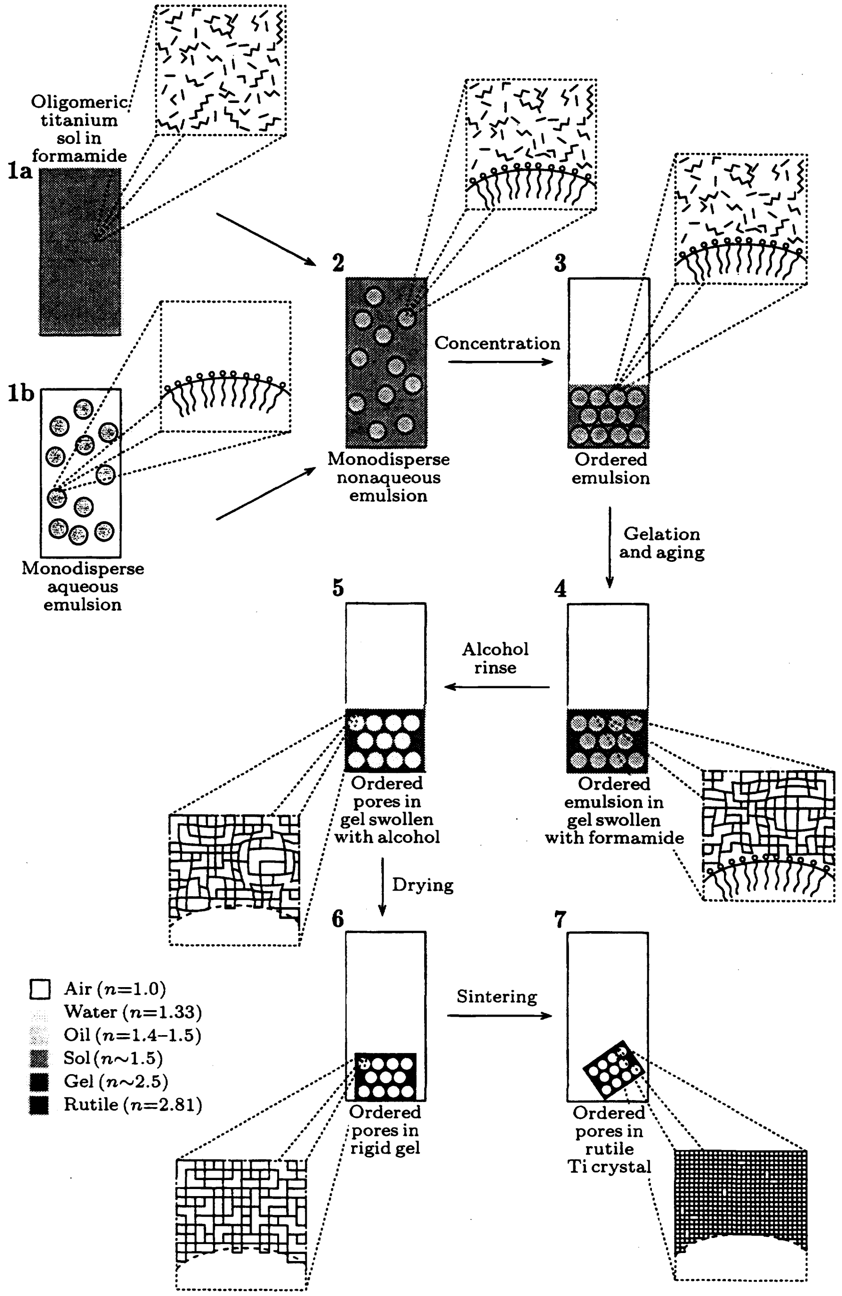

**Figure 2.** Schematic of emulsion templating method used to produce ordered arrays of air spheres in a titania matrix. For each process step, the numbered rectangle shows the arrangement of the macroscopic phases (oil, sol, gel, and so on), while the dashed box shows the arrangement of the molecular species near an interface.

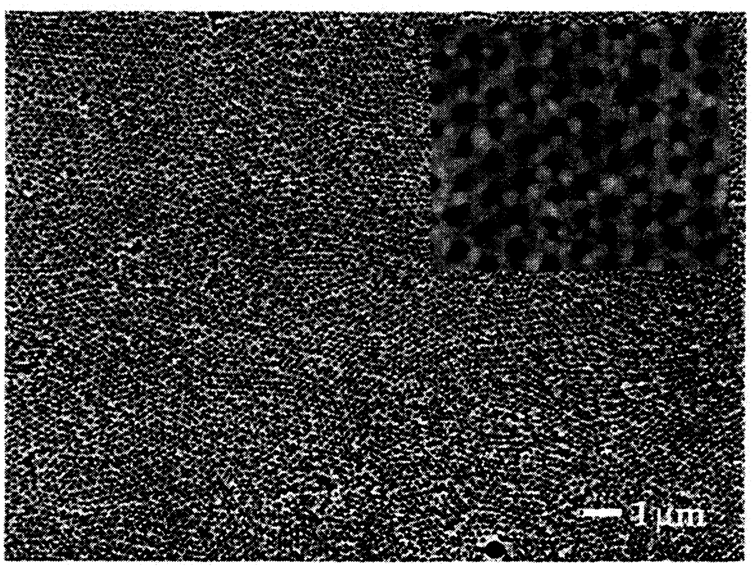

**Figure 3.** Scanning electron micrograph of rutile titania sample with ~200 nm diameter pores. Inset shows 6X magnified view of ordered region. Original emulsion droplet diameter was ~1 µm. Other SEM micrographs (not shown) indicate that the pores are, in fact, closely packed; the picture here shows pores which have been "decapitated" at the surface.

our samples; however, SEM studies indicate that the pore structure is not affected by the grain growth, even though the walls between pores appear rougher at high temperatures. At 1100 °C grain growth leads to degradation of the pore structure.

It is not yet clear why the emulsion templating method can produce macroporous rutile with small grains while other methods, as discussed in Sec. 1, cannot. The anatase-to-rutile phase transition is a metastable-to-stable transition, and as such is extremely sensitive to the synthesis conditions. Changes in alkoxide hydrolysis conditions,[13] chelating agent,[14] and aging time[15] have all been shown to affect the rutile transition temperature and/or crystallite size. The formamide used as solvent in our sample may also have an effect.

We have attempted to achieve a better degree of long-range order by using polystyrene spheres as the template instead of emulsion droplets. The template can be removed in either of two ways: it can be removed just after gelation by rinsing with a solvent for polystyrene, or it can be burned during heat treatment. With either technique we have found that the samples break up into a fine powder after drying. The pore structure after calcination is disordered, and in many cases the rutile grains are very large (>100 nm).

A comparison between the optical transmission spectra for the sample shown in Fig. 3, a rutile sample with disordered pores of a similar diameter (250 nm), and a rutile sample with no pores is shown in Fig. 5. Each sample was prepared and processed in the same way, except that a different emulsion was used in each (no emulsion was used in the nonporous sample). Although the spectrum for the disordered sample is hardly distinguished from the nonporous sample, the ordered sample shows a large, broad minimum that appears to be centered at 500 nm.

One might argue that the minimum in transmission corresponds to the frequency of the pseudo-gap in the calculated density of states[3] for an FCC air sphere lattice with contrast 3:1*. However, such an argument is tenuous since this sample differs from the model used in the calculation in several ways. For instance, the pore arrangement in our sample clearly has several defects and multiple domains, while the calculation has been done for a defect-free lattice. Furthermore in our sample the high dielectric matrix is not uniform but consists of small crystallites of titania. Since the spectrum of a disordered sample with a similar pore diameter does not contain a minimum, we can at least say that the ordering in the sample depicted in Fig. 3 is sufficient to produce photonic band structure.

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*Note that no full band gap should exist for pores this small since such a gap would lie in a frequency range where rutile absorbs strongly.

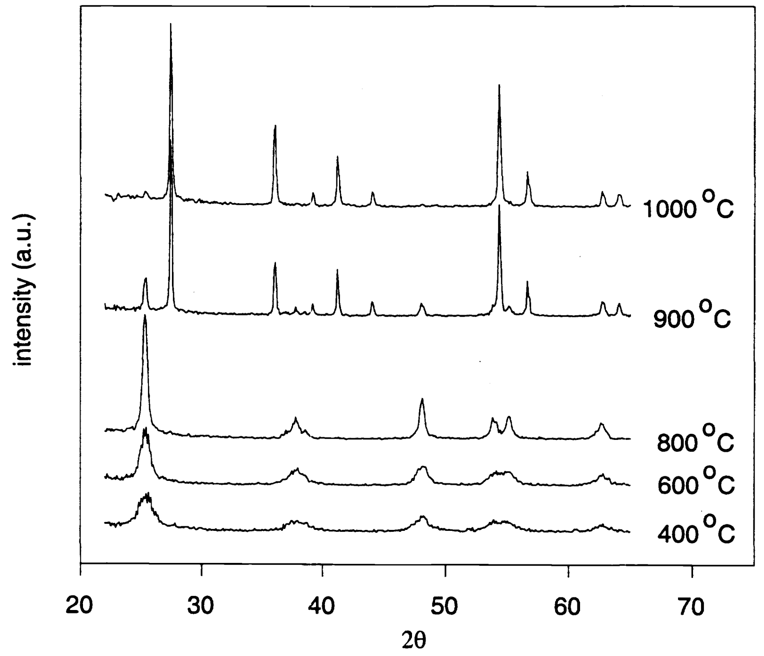

**Figure 4.** Powder X-ray diffraction data for titania samples. Samples were calcined at the temperatures shown for two hours. A maxima at $2\theta = 25°$ indicates the presence of anatase; at $2\theta = 27.5°$, rutile. Transformation from anatase to rutile is complete at 1000 °C.

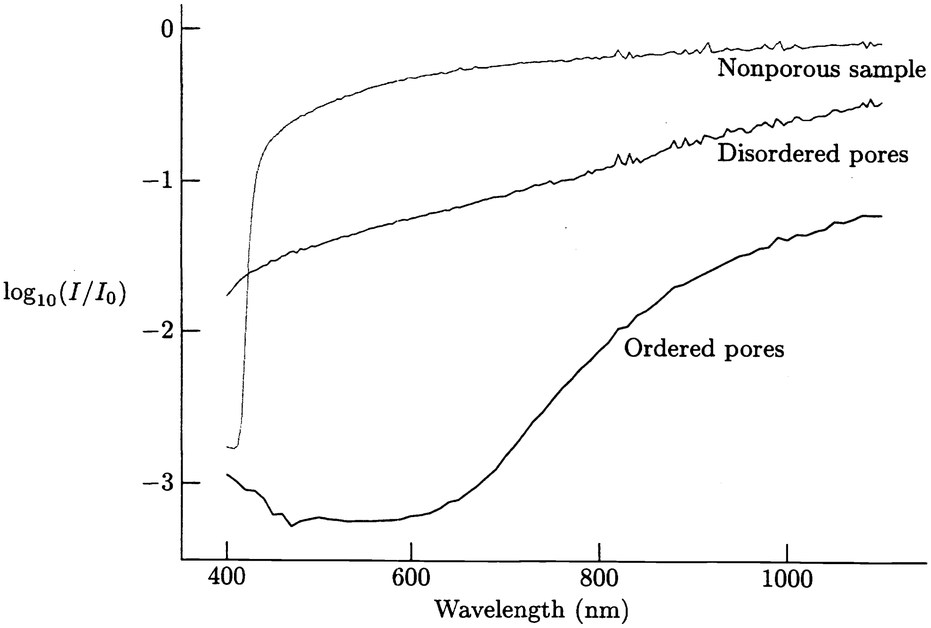

**Figure 5.** Optical transmission intensities (scaled by unscattered intensity $I_0$) versus wavelength for a nonporous titania sample (top), a sample with disordered 250 nm diameter pores (middle), and a sample with ordered 200 nm pores (bottom). All samples were subjected to the same processing route. Sample with ordered pores shows a large dip in the transmission spectrum centered at 500 nm.

## 4. CONCLUSIONS

We have shown that the emulsion templating procedure can produce large samples of macroporous rutile titania with ordered pores. Optical transmission measurements demonstrate that the method holds promise for making photonic crystals with band gaps. The main problem with the current samples is the lack of long-range order in the emulsion crystal. Though our liquid droplets are extremely monodisperse when compared to most emulsions, the polydispersity must be reduced even further (from 15% to below 10%) to compare with polystyrene spheres, which readily form macroscopic colloidal crystals.

The emulsion templating procedure is not limited to titania. In fact, we have used the technique successfully to prepare ordered macroporous silica and zirconia. We expect that the technique is applicable to many other inorganic oxides and possibly polymers. Although titania is the dielectric of choice for optical wavelengths, other materials may be more suitable for applications requiring infrared radiation, for example.

## ACKNOWLEDGMENTS

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