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Colloidal Crystal Approach to the Fabrication of Photonic Band Gap Materials

by

Peng Jiang

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

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Abstract

Colloidal Crystal Approach to the Fabrication of Photonic Band Gap Materials

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Planar single-crystalline colloidal crystals are fabricated by exploiting the spontaneous crystallization of monodisperse silica spheres into close-packed arrays using a convective self-assembly method. Film thicknesses ranging from single monolayers to over 200 layers can be precisely controlled through varying solution concentration and colloid diameter. These high quality periodic arrays exhibit partial photonic band gaps, whose positions and band width depends on the sphere diameters and the number of layers. Their optical transmission is well described by the scalar wave approximation to Maxwell's equations. The thickness dependence of the photonic band gap has also been studied for the first time.

Superlattice colloidal crystals comprised of alternating layers of different sphere sizes can also be formed by the convective self-assembly method. The resulting photonic crystal structures exhibit optical properties which resemble the superposition of the properties of each individual component, with additional structure that suggests the onset of superlattice-type miniband formation. These superlattice structures thus provide a new way to couple light into and out of photonic crystals.

These planar colloidal films are then used as scaffolds to make macroporous materials with crystalline arrays of voids. Macroporous polymers are formed by filling
the interstitial area with monomer which is subsequently polymerized. The silica templates can be removed by etching with hydrofluoric acid. The large voids defined by the silica colloids are not isolated, but rather interconnected by a network of monodisperse smaller pores whose sizes can be controlled by varying the polymerization temperature. These membranes exhibit striking optical properties and their photonic band gap behavior agrees well with theory.

A seeded electroless deposition technique has also been developed for forming macroporous metal membranes. The gold particles attached to the thiol-coated silica colloidal crystals can catalyze the electroless deposition of metals (Ag, Au, Cu, Ni, Co, Pt) inside the arrays and lead to fully dense macroporous metallic films after silica removal. These samples are mechanically robust, electrically active, and possess unusual diffractive optical properties.

The macroporous polymers are again used as hosts to grow a wide variety of complex and unusual colloidal structures. This modern “lost-wax” method effectively capitalizes on the perfection of the starting colloids and the resulting template voids to form monodisperse colloids and their colloidal crystals. A wide variety of highly monodisperse inorganic, polymeric and metallic solid and core-shell colloids, as well as hollow colloids with controllable shell thickness and their colloidal crystals can be made. The polymer template can be uniformly deformed to alter colloidal shape and elliptical particles with precisely controlled aspect ratios are formed for the first time. The hollow sphere titania colloidal crystals exhibit partial photonic band gaps, whose spectral position and width depend on the thickness of the shell and on the overlap between adjacent spheres, in a manner consistent with numerical simulations.
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Introduction

I.1. Photonic Band Gap Materials

The term "photonic band gap" was originally defined in a pair of papers that were published almost simultaneously in 1987. One by Yablonovitch introduced the idea of using forbidden gaps in the photonic density of states as a paradigm for controlling spontaneous and stimulated emission of light;\(^1\) the second by John suggested such gaps would induce Anderson localization of light waves.\(^2\) Both gave a proscription for forming photonic band gap material which possesses a gap. In these three dimensionally periodic dielectric structures, there could exist a band of frequencies over which an electromagnetic wave cannot propagate in any direction, analogous to electronic band gaps in semiconductor crystals. Indeed there was no assurance in 1987 that any photonic band gap materials could ever be produced experimentally with available refractive indexes. The search for a three dimensional (3-D) photonic band gap entailed numerous blind alleys and false starts, culminating in 1990 with the remarkable theoretical discovery that the diamond crystal geometry provided an ideal system for gaps at microwave frequencies.\(^3\) This lead to the first experimental demonstration of a 3-D photonic band gap material.\(^4\) Subsequent experimental demonstration in the microwave domain, have led to extensive theoretical and experimental activity, aimed at the optimization of PBG structures for the visible domain and the exploration of their potential applications.\(^5-7\)
The PBG concept can be viewed as an attempt to bring the design of optical properties to a level comparable with that of electronic properties in modern semiconductor materials. Electrons traveling in a periodic lattice experience a periodic potential. The geometry of the lattice and the strength of the potential cause Bragg-like diffraction effects to arrange the electrons into energy bands separated by gaps in which propagating states are prohibited. Similarly an electromagnetic wave that interacts with a medium having a periodic dielectric function also has certain frequencies which are prohibited from propagating within the material. These gaps in the allowed electromagnetic frequencies are referred to as photonic band gaps. Figure I.1 shows examples of one, two and three-dimensional photonic crystals. Just as control of individual atomic layers and sub-micron patterning have revealed quantum-size effects and paved the way to the development of electronic devices for future high-performance applications, similar control of dielectric material properties on optical-wavelength scales is expected to give rise to a wide range of highly unusual classical and quantum optical effects, that may entail important advantages for optoelectronic devices.

(By courtesy of J. Joannopoulos et al., *Photonic Crystals: Molding the flow of light*, 1995, Princeton Press)

**Figure I.1** Examples of one, two and three-dimensional photonic crystals. The different colors represent different values of the dielectric constant.
Since photonic crystals are classified as materials which have a periodic modulation of their refractive index, this periodicity allows us to use the terminology developed for crystallography to describe the photonic crystal systems. Thus we employ terms such as "Brillioun Zone", "reciprocal lattice" and "band structure" to characterize photonic crystals.

I.2. Fabrication of Photonic Band Gap Materials

As we know from crystallography, electromagnetic radiation scatters off of different lattice planes along different directions of propagation. This anisotropy causes the light propagating through a photonic crystal to experience a direction-dependent periodic potential. So, the band structure will also depend on the propagation vector. Unless the band gaps for all the propagation directions overlap at one frequency, the photonic crystal will not possess a complete band gap; i.e. frequencies for which light propagation is forbidden irrespective of the direction. In order to achieve a complete gap the lattice should have a high degree of symmetry with the Brillioun zone being spherical (for a three-dimensional crystal).\textsuperscript{8} However making such a structure is challenging. Eventually Yablonovitch et al. demonstrated that a material with a diamond structure and a refractive index contrast greater than 2 could form a complete photonic band gap.\textsuperscript{8} Figure I.2 shows this Yablonovite structure, which consists of a dielectric block with a triangular array of holes; each being drilled three times at an angle of 35.26° away from the normal and spread 120° on the azimuth. As the periodicity of the Yablonovite structure is of the order of centimeters, the photonic band gap develops in the microwave wavelength range.
The description of light propagation in photonic crystals involves the solution of Maxwell's equations with a periodic dielectric function. One of the appealing aspects of Maxwell's equations is that there is no fundamental length scale. Thus the solutions are scale invariant, which means that if the Yablonovite structure is scaled down to sufficiently small dimensions (comparable to the wavelength of visible light) a structure is obtained that has a complete band gap in the visible. The most important applications of photonic crystals are in the visible or near-infrared wavelengths. To develop such technologies, like planar waveguides and thresholdless lasers, the fabrication of photonic crystals operational at these wavelengths requires a detailed control over the sub-micron or nanometer length scale. This is a challenging problem for materials fabrication, and two distinct approaches have been explored by the community.

![Diagram](image)

(By courtesy of J. Joannopoulos et al., *Photonic Crystals: Molding the flow of light*, 1995, Princeton Press)

**Figure I.2** The Yablonovite structure consists of a dielectric slab in which a triangular array of holes is drilled. Each hole is drilled three times at an angle of 35.26° away from the normal and spread 120° about the azimuth. This results in a three-dimensional photonic crystal whose (1 -1 0) cross section is shown on the left.
I.2.1. State-of-the-art Lithography Methods

In the first of these approaches, state-of-the-art lithographic methods using techniques originally developed for electronic devices, such as photolithography, electron beam lithography, anisotropic etching and so on have been employed. For example, a woodpile structure has been proposed, which is topologically equivalent to an FCC lattice structure, to exhibit a full photonic band gap.9-11 This type of structure has recently been fabricated using repetitive deposition and etching of multiple dielectric films and demonstrated to have a band gap in infrared wavelengths.12-14. Figure I.3 shows a scanning electron microscopy (SEM) image of a four-layer silicon woodpile structure fabricated by a comprehensive five-level stacking process using advanced silicon micro-electro-mechanical systems (MEMS) and integrated circuit (IC) processes. In their method, within each layer, SiO₂ was first deposited, patterned using photolithography, and etched to the desired depth using plasma etch. The resulting trenches were then filled with polycrystalline silicon. Following this, the surface of the wafers were made flat using chemical mechanical polishing, and the process was then repeated. After the five-level process was completed, the wafer was immersed in a HF/water solution for the final SiO₂ removal. A similar woodpile structure with eight stacking layers has been fabricated exhibiting a full three-dimensional photonic band gap effect at optical communication wavelengths (~1600 nm) by an advanced wafer-fusion technique.15-17 In this method, GaAs strips are stacked with the wafer-fusion and laser beam-assisted very precise alignment techniques. These complex methods using well-developed micro-machining techniques have several advantages, such as the availability of arbitrary morphologies with full 3-D photonic band gaps and the easy introduction of arbitrary defect states into
the crystal. However, the inherent expensive, time consuming fabrication process has low output. In addition it requires specialized instruments and is limited in the number of photonic layers that can be formed. Finally, scaling down dimensions to the visible and ultraviolet wavelengths is problemable.

![Image](image.png)

(By courtesy of Lin et al., *Nature* 394, 251, 1998)

**Figure I.3.** SEM cross-sectional view of a four-layer poly-Si woodpile structure fabricated by the repetitive deposition and etching of multiple dielectric films.

### I.2.2. Colloidal Crystal Methods

Recently, colloidal crystals have received renewed attention as an avenue to achieving controlled dielectric periodicity.\textsuperscript{18-21} Colloidal crystals are regular crystalline arrays of highly monodisperse colloids of dielectric materials such as silica or polymers.\textsuperscript{22} Figure I.4 shows a partial list of these colloidal systems and their typical range of critical dimensions.\textsuperscript{23} The ordered colloids or colloidal crystals have attracted
the attention of physicists for several decades. For example, mineralogical and X-ray studies revealed that precious opal is nothing but a hydrated amorphous form of silica—the most common material on Earth. The iridescent colors of the natural opals are due to the Bragg diffraction of visible light by the 3-D highly ordered submicron silica colloids.

Figure I.5 shows a SEM image of a natural opal.

**Figure I.4.** A list of representative colloidal systems and their typical ranges of diameters.

(By courtesy of R. K. Iler, The Chemistry of Silica, 1979, John Wiley and Sons.)

**Figure I.5.** SEM top-view image of a hydrofluoric acid etched natural opal.
Colloidal crystals offer a starting point for the fabrication of periodic photonic crystals created through self-assembly rather than lithographic means. Here, one has the potential to create samples with full three-dimensional ordering, a feature important for engineering larger and more complete photonic band gaps. Also, self-assembly methods can create thicker materials than those made using lithography. In addition, self-assembly methods are not limited in their length scale, and it is feasible to create materials that are active in the ultraviolet and even the soft x-ray range using colloids with smaller diameters. Finally, as has been demonstrated recently, colloidal crystals provide an ideal scaffold for the creation of both polymeric and inorganic samples with complex porous structures.\textsuperscript{24-33} Such samples may exhibit more complete photonic band gaps than silica-air crystals as higher index contrasts are possible.

The photonic behavior of silica and some polymer latex (such as polystyrene) colloidal crystals have been extensively studied recently, mainly because of the routinely availability of their highly monodisperse colloids. However, these f.c.c. close-packed colloidal crystals do not exhibit full photonic band gaps due to their low refractive index contrast.\textsuperscript{34} Theoretical simulations suggest that high refractive index contrast (\textgreater{} 2.8) is needed to open a full photonic band gap.\textsuperscript{34} To achieve high index contrast, these colloidal crystals must be filled with other high refractive index materials, such as TiO\textsubscript{2} and polycrystalline silicon.\textsuperscript{27,33} Subsequent selective removal of the templates produces high refractive index materials with highly 3-D ordered air spheres, called inverted opals. Full 3-D photonic band gaps near 1.5 micrometers have recently been demonstrated in the macroporous silicon samples that are templated from silica colloidal crystals using chemical vapor deposition of silicon.\textsuperscript{33} Figure I.6 shows a SEM image of a macroporous
silicon sample. Inverted opals provide a very economic route to the fabrication of photonic crystals with a complete 3-D band gap in the infrared and visible wavelengths in large scale.

![SEM image of a macroporous silicon sample.](image)

(By courtesy of Blanco et al., *Nature* 405, 437, 2000)

**Figure I.6.** SEM image of a macroporous silicon sample.

### I.3. Applications of Photonic Band Gap Materials

Photonic technology, using light instead of electrons as a unit of information, is increasingly replacing electronics in communication and information management systems. Light has several advantages over the electron. It can travel in a dielectric material at much greater speeds than an electron in a metallic wire. Light can also carry a large amount of information per second. The bandwidth of dielectric materials is significantly larger than that of metals. Furthermore, photons are not as strongly interacting as electrons, which helps reduce energy losses.

The absence of any propagating modes in a photonic crystal can suppress spontaneous emission for photons with frequencies within the gap.\(^1\) The ability to confine and control light in three dimensions would have important implications for
quantum optics and quantum-optical devices: the modification of black-body radiation, the localization of light to a fraction of a cubic wavelength, and thus the realization of single-mode light-emitting diodes, are but a few examples. Photonic crystals can also be used in frequency selective mirrors, band-pass filters and optical resonators. By introducing controlled line or point defects in the photonic crystals one can observe localization of electromagnetic waves leading to the fabrication of planar waveguides for all-optical circuits, that can bend at sharp angles (even 90°), and thresholdless lasers. Thus, photonic crystals may pave the way for a new technological revolution analogous to the development of semiconductor technology 50 years ago.
References


Chapter 1

The Fabrication and Photonic Band Gap Properties of Single-
Crystal Colloidal Crystals of Controlled Thickness

Introduction

Many novel properties can be engineered in periodic dielectric materials by controlling the symmetry and length scale of a samples' microstructure.\textsuperscript{1-6} This idea has been used to engineer microwave optics,\textsuperscript{4} and recently these dielectric structures have been termed "photonic band gap" materials.\textsuperscript{12,16,17} The exciting potential of these structured materials for optical applications has motivated efforts to shrink the length scale of their periodicity to sub-micron sizes.\textsuperscript{7-17} Lithographically prepared arrays of alumina rods, for example, were recently used as a planar waveguide device operating in the gigahertz;\textsuperscript{4} alternating layers of AlGaAs and AlAs deposited through chemical vapor provide a stacked dielectric cavity used in distributed feedback lasers.\textsuperscript{18} While these methods for creating dielectric structures have found use in commercial products, the potential applications of photonic band gap materials at optical wavelengths have been limited by the difficulty in fabricating three-dimensionally periodic materials with nanometer-scale structure.

Recently, colloidal crystals have received renewed attention as an avenue to achieving controlled dielectric periodicity.\textsuperscript{19-22} Colloidal crystals are regular crystalline arrays of highly monodisperse spheres of dielectric materials such as silica or
polymers. These materials have been the subject of study for several decades due to their unusual optical and thermodynamic properties. Colloidal crystals offer a starting point for the fabrication of periodic dielectric materials created through self-assembly rather than lithographic means. Here, one has the potential to create samples with full three-dimensional ordering, a feature important for engineering larger and more complete photonic band gaps. Also, self-assembly methods can create thicker materials than those made using lithography. While the role of sample thickness in the optical properties of colloidal crystals has not been investigated, it is clear that control over this important parameter would be quite valuable in materials engineering. In addition, self-assembly methods are not limited in their length scale, and it is feasible to create materials that are active in the ultraviolet and even the soft x-ray range using colloids with smaller diameters. Finally, as has been demonstrated recently, colloidal crystals provide an ideal scaffold for the creation of both polymeric and inorganic samples with complex porous structures. Such samples may exhibit more complete photonic band gaps than silica-air crystals as higher index contrasts are possible; in addition, they also may find applications in catalysis and separation technologies. The success of these non-lithographic routes to the formation of periodic dielectric structures requires the development of robust methods for creating high quality, uniform, mechanically stable colloidal crystals.

A popular method for creating colloidal crystals is by gravity sedimentation of colloids from dispersions; recent progress in the area has focused on strategies for strengthening the crystals and generating sample formats well suited for optical testing. In one instance, silica colloids were crystallized between parallel plates and the
solvent was then polymerized so as to trap their crystalline order.\textsuperscript{47-49} This stabilization comes at a cost, however, as the matrix material has a refractive index closely matched to the colloids, thus reducing their diffractive properties. In other work, silica colloids were crystallized in capillaries and the solvent was allowed to evaporate. The resulting silica-air structures have strong diffractive properties and transmission spectra can be collected over some regions.\textsuperscript{50} Nonetheless, gravity sedimented samples generally contain polycrystalline domains of unknown sizes.\textsuperscript{51,52} In addition, during the gravity sedimentation method crystal formation can only occur at specific volume fractions of colloids.\textsuperscript{23} As a result, array growth is difficult to adjust, and thus film thickness is not easily controlled.

Other methods for ordering colloids into arrays have been explored by investigators seeking to make dense monolayer films of close-packed colloids for non-optical applications. Under the right conditions, colloid solutions that are spun-coat onto surfaces provide high quality monolayers.\textsuperscript{53-57} Convective self-assembly of wetting solutions is also a route for making ordered monolayers and structures of nanocrystals on a variety of substrates.\textsuperscript{58} Another method applied to polymer colloids uses the flow of solvent through micromachined channels to create dense colloidal arrays of multiple layers.\textsuperscript{38,39,59,60} Finally, recent work by Nagayama et al.\textsuperscript{61-70} has exploited capillary forces to drive the assembly of larger (d > 1 \textmu m) polystyrene colloids on flat surfaces. This method, which is conceptually similar to the Langmuir-Blodgett methods for film deposition, creates ordered monolayer films on nearly any vertical surface. Under the appropriate solvent and colloid conditions Nagayama et al. showed that patches of bi- and tri-layer arrays could also be formed. All of these methods have the advantage of
producing well-ordered films on planar surfaces quite rapidly; however, in most instances the deposition techniques have been optimized for the formation of monolayer films.

In this chapter a self-assembly technique which relies on capillary forces to organize colloids is used to fabricate colloidal crystal multilayers.\textsuperscript{71} These arrays are ordered over long (~1 cm) length scales and can be fabricated in a single deposition with thicknesses ranging from two layers to several hundred layers. Moreover, the thickness of the resulting sample can be precisely dictated through control of sphere size and concentration in solution. This deposition behavior can be adequately simulated using existing models of film formation developed for monolayer samples. The resulting planar colloidal crystals are highly ordered, and evaporation of the solvent leaves a silica-air array with good optical contrast and mechanical stability. The optical properties of these samples are measured at normal incidence and their qualitative features and trends compared to gravity sedimented colloidal crystals. In addition, the thickness dependence of the optical properties of these periodic planar arrays of submicron silica spheres is studied and compared to the predictions of the scalar wave approximation.

**Experimental Section**

**Materials and Substrates.** All solvents and chemicals are of reagent quality and used without further purification except for tetraethoxysilane (99\%, Alfa) and 3-(trimethoxysilyl)propyl methacrylate (TPM, 98\%, Aldrich) which are freshly vacuum distilled before use. 200 proof ethanol is obtained from Pharmaco Products and 29.6\% ammonium hydroxide is purchased from Fisher. Ultrapure water (18.2 MΩcm\textsuperscript{-1}) is used directly from a Milli-Q water system. Microslides (75 × 25 × 1 mm, Fisher) are cut into
two equal halves along the long sides and are used as substrates. Glass scintillation vials (20 mL, Fisher) are used as experimental cells.

**Instrumentation.** Scanning electron microscopy is carried out on a software-controlled LEO 440 SEM designed specifically for electron-beam lithography and a Philips XL30 ESEM. Transmission spectra are obtained using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer. A Coulter N4 Plus Laser Dynamic Light Scattering (DLS) is used to size the particles. A CrC-100 sputtering system is used to sputter a thin layer (3-4 nm) of gold on samples before SEM analysis.

**Submicron Silica Colloids Synthesis.** Monodisperse SiO₂ nanospheres are synthesized following the Stober-Fink-Bohn method by the hydrolysis and condensation of tetraethoxysilane (TEOS) in the presence of water and ammonia. Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviation smaller than 7% are obtained through strict control of the reaction conditions. The purity of the reagents is found to be critical to the final size distributions of the synthesized silica colloids. All the solvent (200 proof ethanol) and reagents (water and 29.6% ammonia) except for TEOS which is vacuum distilled prior to use, are filtered through 0.2 µm syringe filters (Gelman Sciences). In general, a 250 mL Erlenmeyer flask is soaked in a bath base and then a 2% hydrofluoric acid solution both for eight hours. Then the flask is thoroughly washed using Milli-Q water (18.2 MΩcm⁻¹) and dried in a 120°C oven for overnight. The flask is sealed with a pre-cleaned septum (No. 49, Aldrich) and purged with dry nitrogen gas for 15 minutes. Then the calculated amounts of 200 proof ethanol, Milli-Q water and ammonia are injected into the flask through 0.2 µm syringe filters. Finally, distilled TEOS is quickly injected into the stirred solution and the solution is
continually stirred for eight hours in moderate speed. The synthesized silica can be stored in the sealed Erlenmeyer flasks for several years. The sizes and size distributions of these samples are obtained from SEM and DLS measurements. Over 200 spheres are sized using SEM in order to arrive at the reported diameters.

**Colloid Purification.** Before deposition, the silica alcosols are washed with 200 proof ethanol by repeated centrifugation (4200 rpm) and ultrasonic dispersion cycles in order to remove impurities, such as ammonia, water and unreacted TEOS. Six cycles are usually performed. The final centrifugation cakes are redispersed in 200 proof ethanol and the purified silica alcosols can be stored in sealed bottles for over years.

**Experimental Apparatus and Procedures.** Prior to use all microslides and scintillation vials are soaked in chromic-sulfuric acid clearing solution overnight, rinsed well with ultrapure water from Milli-Q water system, and dried in a stream of nitrogen. A clean microslide is then placed into 15 mL of purified silica alcosol in a clean scintillation vial. The vial is covered by a 1200 mL crystallizing dish to keep out external airflow and contamination. The entire apparatus is placed on a vibration-free bench in a

![Diagram of experimental apparatus](image.png)

**Figure 1.1.** Experimental apparatus for the fabrication of silica colloidal crystals.
temperature-controlled laboratory (22°C, ± 1°C). The experimental apparatus is shown in Figure 1.1. For the preparation of these multilayer samples no substrate withdrawal is necessary.

The volume fractions of different samples are determined by drying 6 mL purified silica alcosol in 80°C vacuum oven overnight and then weighing the residual solid. 2.04 g/mL is used as the density of silica,73 though its actual density may be somewhat lower. Then, the samples are diluted or concentrated using a centrifuge-redisperse cycle to the required volume fractions.

For evaluation of the role of sphere size on film formation, six samples (215.2 nm (3.9%), 298.6 nm (3.8%), 324.1 (7.2%), 396.6 nm (5.4%), 437.4 nm (4.2%), 508.6 nm (4.3%)) were used. Numbers in parentheses following the sphere diameters refer to the relative standard deviation of the measured diameters. All the samples were placed under the same crystallizing dish to ensure identical ethanol evaporation rates. Samples with volume fractions of 0.1%, 0.5%, 1.0%, 1.5%, 2.0%, 3.0% and the same particle size (298.6 nm (3.8%)) were used to determine the effect of volume fraction on the film thickness. Samples (215.2 nm (3.9%) and 279.2 (4.6%)) with volume fractions of 1% were used to determine the effect of solvent evaporation rate on the film thickness. Duplicates of each sample were tested under three different evaporation conditions: open to ambient atmosphere, covered in a crystallizing dish, and covered in a crystallizing dish with small amount of ethanol (20 mL in a 50 mL beaker). One of the duplicates was used to determine the evaporation rate by weighing the vial on a digital analytical balance. The typical solvent evaporation rate, given in units of volume per time, was found to be 9×10⁻⁴ cm³ per minute.
Thicker films are fabricated by successive dip coating. After each single coating is deposited, the film is air-dried for at least 24 hours and dipped again into another purified silica alcosol with the same particle size. The coating and drying cycle can be repeated to systematically increase film thickness.

**Characterization of the Silica Colloidal Crystal Films.** Scanning electron microscopy (SEM) is used to determine the film thickness. Samples are scraped using a sharp razor blade, and a thin layer of gold is sputtered onto the samples prior to imaging. By tilting the specimen 30-40° it is possible to image the edges of the films, and thus obtain a perspective cross-sectional view. In order to quantify film thickness and variation from such images, ten random locations in an edge are analyzed. These data are collected from the center square centimeter of the sample. Optical properties of the silica colloidal single crystal films are evaluated by measuring their transmission spectra at normal incidence, using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer.

**Results and Discussions**

Crystalline quality is among the most important parameters in determining the performance of colloidal crystals in optical applications. The formation of point defects or domains can have an enormous impact on the diffraction properties. Figure 1.2A shows a typical SEM image of a single crystal of colloidal silica with 298.6nm diameter, grown using the methods described above. This sample exhibits an ordered closed-pack arrangement of silica over a sample area of 10 μm. This ordered arrangement extends over a much longer range; this can be illustrated by two-dimensional Fourier transform of a low-magnification SEM image. Such data is shown in the inset of Figure 1.2A. The
sharp peaks confirm the presence of long-range crystalline order, extending over the largest length scales (40×40 μm²) accessible in a single low-magnification image.

Figure 1.2. (A) Typical scanning electron micrograph (SEM) of a sample (top view) showing spheres of 298.6 nm diameter. The inset shows a Fourier transform of a 40×40 μm² region. B) Typical SEM side view of the same sample at the same magnification (×12,000), showing a perspective view of the cleaved face and the underlying substrate.
Perfectly ordered films can be made for a variety of sphere diameters. Figures 1.3A and 1.3B show SEM images of two crystals with different particle sizes (206.4 nm and 437.4 nm, respectively). As in Figure 1.2A, long range order is confirmed by Fourier transform of low magnification images (insets to Figure 1.3).

Figure 1.3. SEM images of 2 samples with different particle diameters (×12,000 magnification). The insets show Fourier transforms of 40×40 μm² regions. (A) d = 206.4 nm. (B) d = 437.4 nm.
Evidence of sample order over even longer length scales is challenging as lower magnification images do not have the spatial resolution needed to identify distinct colloids; one approach is to compare micrographs of 40 \( \mu \text{m}^2 \) areas collected as a sequence during the translation of the sample. If domain boundaries are observed during this movement, then the hexagonal registry of the images evident in their FFTs will not be aligned. Figure 1.4 shows such data for four representative images taken at the edges of a 4 millimeter square. The alignment of the spots in all four images illustrates the registry of the array lattice over these long length scales. Moreover, analysis of many intermediate images also showed perfect alignment and no evidence of any grain boundary.

**Figure 1.4.** Fourier transforms (FFT) of four 15.75 \( \times \) 11.75 \( \mu \text{m} \) regions of a 1 cm\(^2\) colloidal silica single crystal. These images were part of a series taken every 50 microns over a 4\( \times \)4 mm square region; they represent the four corners and image (c) was closest to the edge of the sample. The four parallel dashed lines indicate one reference direction, and demonstrate that the four images are roughly of the same orientation, as were all intermediate images. Within a 4 \( \times \) 6 mm\(^2\) region, the largest deviation from this orientation is \( \sim 1.6 \) degrees, represented in (c). This demonstrates that the crystallographic orientation of the sample is preserved over this entire region.
While order within the plane parallel to the glass substrate is important for the optical properties of the films, especially when evaluated away from normal incidence, the stacking of close-packed layers perpendicular to the substrate is responsible for the diffraction observed in normal-incidence transmission measurements. To evaluate this issue, colloid films can be abraded to reveal their stacking perpendicular to the substrate as shown in Figure 1.2B. This cross-section shows that the close-packed structure extends uniformly over the 15 layers shown; Figure 1.8b shows a thicker 50 layer sample which also exhibits a regular arrangement from the top surface to the bottom surface. The high uniformity of the films' order and thickness is also evident in their uniform appearance (see Figure 1.5).

Figure 1.5. (A) Photograph of three samples with different sphere diameters (307.2 nm, 353.0 nm and 383.7 nm, from left to right). The samples are clear and highly uniform. (B) Photograph of the same samples illuminated with a white light source.
To form high quality planar crystals, particle size distribution is a crucial factor. This is illustrated in Figure 1.6, which shows SEM images of two samples with different size distributions (3.8% and 14.2% relative standard deviation, respectively). The sample

Figure 1.6. SEM images of 2 samples with different particle size distributions (×12,000 magnification). The insets show Fourier transforms of 40×40 μm² regions. (A) S.D. = 3.8%. (B) S.D. = 14.2%. 
with a narrow size distribution exhibits order over a long length scale and sharp peaks in the Fourier transform of a low-magnification SEM; the polydisperse sample has only short-range order and exhibits rings in the Fourier transform. Films that lack crystalline quality, such as the one shown in Figure 1.6B, even when relatively thin, are white and opaque. This is in sharp contrast to the brilliant color and transparency apparent in more ordered films (Figure 1.5). Data collected from over twenty samples suggests that colloids must have a size distribution with relative standard deviation less than 8% (on the diameter) in order to form high quality close-packed crystals, and thus good optical samples, using this method.

For this deposition process, two parameters allow for control over film thickness (or number of colloidal layers): particle radius and particle volume fraction. Figure 1.7 shows how film thickness varies with these two parameters. For these measurements layer thickness is determined using cross-sectional SEMs of the types shown in Figures 1.1B, 1.7, and 1.8. Particle size affects the film thickness in a systematic way: for the same volume fraction, a solution of larger particles yields thinner films. Two examples are shown in Figure 1.7, and the relationship is quantified in Figure 1.9A. Particle volume fraction also affects film thickness (Figure 1.9B); more concentrated colloidal solutions leave thicker multilayer deposits (Figure 1.8). Because film uniformity degrades significantly when colloidal solutions of more than 4% volume fraction are used, the formation of thicker films requires multiple coating. In this approach, samples are allowed to dry and then are reimmersed in the colloidal solutions; new colloidal multilayers form easily on top of the original ones and the process can be repeated many
times with the thickness increasing linearly after each deposition. Figure 1.10 shows a scanning electron micrograph of a portion of a multicoated sample.

Figure 1.7. SEM cross-sectional images of two samples with different particle diameters, grown from solutions with the same volume fraction (0.5%). The 206.4 nm particle size produced a film with 14 layers (A) and a 396.6 nm particle size produced a film with 7 layers (B).
Figure 1.8. SEM cross-sectional images of two samples grown from solutions with different particle volume fractions. In both (A) and (B), the spheres are 298.6 nm in diameter. (A) V.F. = 0.8%, 18 layers. (B) V.F. = 3.0%, ~50 layers.
Figure 1.9. (A) Number of layers versus the inverse of the particle diameter, for samples grown from a 1% volume fraction solution. (B) Number of layers versus the particle volume fraction. In both (A) and (B), the spheres are 298.6 nm in diameter.
Figure 1.10. Typical SEM image of a sample (d = 279.2 nm) deposited with four successive coatings. Each deposition provides 12 colloidal monolayers.

The optical properties of these films can be evaluated using visible-near-IR transmission in normal incidence. Figure 1.11 shows scaled absorption spectra versus particle size for a wide range of colloidal sphere diameters. Two notable features of the spectra are sharp peaks due to the Bragg diffraction of visible light from the ordered spheres, and a background rising at shorter wavelengths. The systematic change in color seen in transmission and reflection of uniform films of different particle sizes (see Figure 1.5) is due to Bragg diffraction. Figure 1.12 shows the changes in the optical
transmission spectrum of films of different thicknesses made from the same particles. The background has been subtracted in these data so that they can be compared easily. The intensity of the diffracted peak increases approximately linearly with the number of layers, although this is not evident in Figure 1.12 because the data have been scaled to uniform height. Also, the peak widths narrow as sample thickness is increased. Finally, Fabry-Perot fringes (indicated by the arrows in Figure 1.12) become smaller and more closely spaced in thicker samples.

![Graph](image)

**Figure 1.11.** Normal incidence transmission spectra (optical density) of samples with different sphere diameters, determined using SEM analysis. These curves have been scaled to a constant height, and vertically offset for clarity. The arrows indicate the expected positions of the peaks for each curve, calculated using Bragg's law at normal incidence and the diameters shown. Typically, at the peak maximum only 10-20% of the incident light is transmitted.
Figure 1.12. Normal incidence transmission spectra (optical density) of three samples (d = 279.2 nm) with increasing film thickness. These curves have been scaled to a constant height, and vertically offset for clarity. Thicker samples exhibit more closely spaced (and smaller) Fabry-Perot fringes. The arrows indicate local maxima, \( \lambda_p \), chosen for analysis, with the longest wavelength as \( p = 0 \) (see Figure 1.13 and 1.14). In addition, a rising background apparent in the data of Figure 1.11 has been subtracted from this data; for samples of more than 20 layers, this background contributes at most 20% of the rejection of light at the peak maximum.
Characterization of Colloidal Crystal Films

*Crystal Structure of Planar Arrays.* SEM images of the top view of these samples show that the colloids are arranged in a close-packed fashion, with each sphere touching 6 others in one layer (Figures 1.2 and 1.3). This close-packing arrangement is well known in crystals comprised of colloids, such as these silica spheres, whose ionic interactions are minimal.\textsuperscript{74,75} In this close-packed geometry, whether the structure is face-centered cubic (ABCABC...), hexagonal close-packed (ABABAB...) or randomly packed, these images illustrate that the samples are oriented with their (111) axes parallel to the substrate.

Exact characterization of the crystal structure of these samples from SEM micrographs alone is problematic. Though images such as these confirm a regular close-packed arrangement (Figures 1.2B, 1.7, and 1.8), they cannot be used to distinguish between the f.c.c. and h.c.p. structures. This is because it is difficult to determine the exact angle of the cross-sectional view, which in turn makes it difficult to assess which crystal face is visualized in these images. Confocal microscopy of gravity sedimented colloidal crystals\textsuperscript{76} has indicated that the stacking between (111) planes is neither f.c.c. nor h.c.p., but a random arrangement. Theoretical calculations, though, have indicated that the f.c.c. structure is stabilized slightly even with completely non-interacting spheres.\textsuperscript{77,78} In future studies, where the transmission is investigated as a function of angle away from the normal, the exact nature of the crystal structure will be a more important issue.\textsuperscript{27,28}

*Domain Size of Planar Arrays.* An important feature of these samples is their long-range order within the plane parallel to the substrate. In gravity sedimented
colloidal crystals there can be some preferential alignment of the crystal axes with the capillary sidewalls; however, these samples are multicolored under white light illumination\textsuperscript{79} and are thought to contain colloidal crystal domains whose (111) axes are not aligned. In contrast, the multilayer samples described here are deposited onto a flat substrate which forces their (111) axes to be aligned over distances of millimeters (Figure 1.2B, Figure 1.4). For this reason, when viewed at a variety of angles, the color of the entire film is uniform (Figure 1.5). Thus, unlike the gravity sedimented colloidal crystals which are polycrystalline in most instances,\textsuperscript{51,52} these samples consist of a single crystalline close-packed array.\textsuperscript{80} We note that in this work when samples with slightly broader size distributions (> 8%) are deposited, grain boundaries in the plane parallel to the substrate are observed; similarly, Nagayama et al. observed grain boundaries in monolayers of colloids with 10% to 15% distributions in size.\textsuperscript{62} This suggests that the monodispersity of the colloids, rather than the deposition process itself, is responsible for their long range ordering.

\textit{Perfection of Colloidal Crystals.} Though these samples are single crystals, they are not perfect crystals as is clear from the SEM photographs. Two types of defects are observed routinely in the SEM images of these samples. The first are sphere vacancies that appear every ~10 microns on average. The second are vertical cracks in the crystal, perpendicular to the glass substrate. Examples may be seen in Figures 7 and 8A. Cracks are typically observed every 10 microns in most samples and unlike a classic grain boundary, the registry of the hexagonal packing is preserved across these features. One explanation for the cracking is that the deposition of metal and the subsequent exposure of films to the high vacuum of the SEM damages their structure and induces cracking; to
evaluate this issue, atomic force microscopy (AFM) of the same materials was performed under ambient conditions on the as-prepared surfaces. Though cracks were still observed, they were far fewer, typically found every 100 microns. The drying tension in thin colloidal films is well known to cause cracking of much thinner deposits;\textsuperscript{81} it is likely that such drying-induced shrinkage is responsible for this problem as well. Strategies for minimizing this effect include the addition of surfactants, and better control over the drying conditions.

**Controlling Film Thickness**

One of the great advantages of using this method of colloidal crystal formation is its ability to create samples with precisely controlled thickness. By controlling such parameters as colloidal concentration and sphere size it is possible to vary the thickness of the films from a few layers to hundreds of layers. The representative images in Figures 1.7 and 1.8 suggest that film thickness, $T$, is related to the deposition parameters in a systematic way. Figure 1.9 illustrates the quantitative relationships between the number of colloidal layers, $k$, and the deposition parameters $\varphi$ (volume fraction of colloids in solution) and $d$ (colloid diameter).

These trends can be understood using a model developed by Nagayama et al.\textsuperscript{61-70} for the self-assembly of *monolayer* colloidal films. In his experiments, which are reminiscent of Langmuir-Blodgett methods for self-assembly, a vertical or slanted substrate is withdrawn from a solution of polystyrene colloids at a constant rate. A meniscus region is formed on the substrate due to wetting by the solution; evaporation of the solvent out of this thin meniscus leads to a constant solution influx, which draws colloids into the area of film formation. During the solvent evaporation these colloids
experience interparticle capillary forces which organize them into close-packed arrays. The resulting thickness is then entirely dependent on the flux of particles into the meniscus, and mass balance can be used to derive a simple formula for array thickness. The profile of growing monolayer particle arrays from a bulk suspension onto a flat substrate plate in the vicinity of the array's leading edge is schematically shown in Figure 1.13.

![Diagram of particle and ethanol fluxes](image)

**Figure 1.13.** Sketch of the particle and ethanol fluxes in the vicinity of monolayer particle arrays growing on a substrate plate that is being withdrawn from a suspension. The inset shows the menisci shape between neighboring particles.

The film formation conditions used by Nagayama et al. were optimized for the production of uniform colloidal monolayers; however, it is possible to adapt this formalism to the formation of the multilayer films that are the subject of this chapter. In
order to create thick films, the array growth rate, which is a balance of the solvent evaporation and substrate withdrawal rates, must be as small as possible. Thus, the slowest possible array growth results when the substrate is not mechanically withdrawn. Under this circumstance the array growth rate and the solvent evaporation rate are equal. This leads to a prediction that the final multilayer thickness depends on the deposition parameters according to:

\[ k = \frac{\beta L \phi}{0.605 d (1-\phi)} \]  

[1]

where \( k \) is the number of layers, \( L \) is the meniscus height, \( \beta \) is the difference between the velocity of a particle in solution and the fluid velocity and is taken to be 1, \( d \) is the particle diameter and \( \phi \) is the particle volume fraction in solution. This equation was derived from the equation 7 from Nagayama et al.\textsuperscript{62} by allowing the evaporation rate, \( j_e \), to be equal to the array growth rate, \( \nu_c \). The data shown in Figure 1.9 clearly demonstrates that the basic trends predicted by this equation are valid. A surprising result from the model is that the final array thickness is not dependent on the solvent evaporation rate. This is because, while faster solvent evaporation does lead to faster array formation, it also leads to increased solution influx into the array growth region. This increased influx of silica colloids balances the faster growth rate leading to a film thickness independent of evaporation rate. This prediction was verified experimentally by creating multilayer samples under different evaporation conditions. While film uniformity was somewhat dependent on evaporation rate, film thickness was not. In addition, film thickness was insensitive to the surface derivatization of the colloids.

An important issue in this method is the role that the solvent plays in controlling the deposition of colloidal multilayers. The solvent enters into the model through the
parameter \( \ell \) that is defined as the height of the meniscus over which evaporation occurs. In the case of the ethanolic solutions used in this work, this parameter can be extracted from linear fits to the data shown in Figure 1.9. Assuming a \( \beta \) of 1, the data in Figure 1.9A provides an \( \ell \) value of 316 microns while the data in Figure 1.9B gives an \( \ell \) value of 301 microns. Similar evaporation lengths, on the order of 200 microns, were reported for the growth of polystyrene colloidal monolayers from water.\(^{68}\) While this parameter cannot be exactly computed, an upper limit for its value can be found by considering the meniscus height of ethanol on a flat glass surface. Using the surface tension of ethanol, and its contact angle for wetting glass, it is possible to calculate a meniscus height of 3500 microns.\(^{82}\) As expected, the observed meniscus height of \(~ 310\) microns is smaller than the value for a flat substrate as the film must wet a rough surface of colloids. This analysis suggests that solvents such as water which have large surface tensions and even lower contact angles should deposit thicker films than the corresponding ethanolic solutions. Attempts to deposit silica colloids from aqueous solutions did lead to thicker films, but these samples had poor uniformity.

**Measuring Multilayer Thickness Using Optical Techniques**

Multilayer thickness is an important parameter for quantitative assessment of sample optical properties. While scanning electron microscopy (SEM) provides a measure of this parameter, and is the only method of thickness determination used in this work, it is a destructive method as it requires a thin gold coating on the sample. A non-destructive technique which requires less time would be of great value. For this purpose, the Fabry-Perot (FP) fringes\(^{83}\) can be analyzed to determine film thickness. These fringes result from interference between reflections from the top and bottom surfaces of the sample and
are indicated by the arrows in Figure 1.12. Thus an analysis, using Bragg’s Law, of the spectral positions of these local maxima permits an accurate determination of sample thickness as shown in Figure 1.14. At normal incidence, one particular FP maximum (e.g., the one at the longest wavelength) occurs at a wavelength, \( \lambda_l \) given by:

\[
p_l \lambda_l = 2 n_{\text{eff}} T. \tag{2}
\]

Here, \( p_l \) is an integer, \( n_{\text{eff}} \) is the effective refractive index of the medium and \( T \) is the film thickness. Subsequent maxima appear at shorter wavelengths:

\[
(p + p_l) \lambda_p = 2 n_{\text{eff}} T. \tag{3}
\]

\( p \) is a positive integer numbering consecutive maxima from the long-wavelength fringe, \( p_l \). Rearranging equations (2) and (3) gives the film thickness, \( T \):

\[
T = \frac{p \lambda_p \lambda_l}{2 n_{\text{eff}} (\lambda_l - \lambda_p)} \tag{4}
\]

The thickness determined from this optical technique is in excellent agreement with thickness found from cross-sectional SEM as shown in Figure 1.15.
\[ 2n_{\text{eff}} \frac{(\lambda_p - \lambda_0)}{\lambda_p \lambda_0} \times 10^3 \]

**Figure 1.14.** Fringe order, \( p \), versus weighted maxima position, for samples of two different thicknesses.
Figure 1.15. Correlation between film thickness estimated by SEM and by Fabry-Perot fringe analysis. The FP analysis provides a layer count by dividing the thickness (\(T\)) by the close-packed plane spacing. From this data, it is evident that the Fabry-Perot thickness measurement method is sufficient to quantitatively determine the thickness of ordered colloidal thin films (solid line has a slope of 1). This technique cannot measure film thickness greater than 8 \(\mu\text{m}\) when using visible light. The amplitude of the Fabry-Perot fringes decreases with increasing film thickness, eventually becoming too small for measurement.
Thickness Uniformity in Multilayer Samples

An important feature of this deposition method is that it allows for the systematic control over multilayer thickness (Figure 1.9). Indeed, the preparation of such well-controlled materials now makes it possible to evaluate many thickness-dependent properties of these systems. For this work to proceed, however, it is important to assess the uniformity of the film thickness over the entire area of the sample. One way to characterize the thickness distribution is to rely on the statistical analysis of cross-sectional SEM images. Films are typically abraded along a diagonal and it is possible to collect cross-section data at many points over the entire central region (~5mm) of the sample. The standard deviation in these measurements is on the order of 10%. A complementary method for analyzing film thickness uniformity is to rely on the optical techniques to assess film thickness (Figures 1.14 and 1.15). Simulations of the interference effect indicate that if the thickness of the sample in the optical path varies by more than ±10%, then well defined maxima and minima will not be observed. Thus, the observation of well-defined fringes (Figure 1.11) demonstrates that film thickness deviates less than 10% on average.

The Thickness Dependence of the Optical Properties of Colloidal Multilayers

The basic features of the normal incidence optical spectrum of these colloidal crystal multilayers are in good agreement with those observed for gravity-sedimented samples. Figure 1.11 shows how the peak in the optical spectrum depends on sphere diameter. When the wavelength of incident light satisfies the Bragg condition, it is diffracted away from the propagation axis leading to a decrease in the transmission and thus a peak in the absorption spectrum. The position of this peak can be related to the
sphere diameter and the effective refractive index of the medium using \( \lambda_{\text{max}} = 2 n_{\text{eff}} d_{111} \), where \( d_{111} \) is the interlayer spacing. For close-packed spheres, the interlayer spacing is related to the sphere diameter, \( D \), by \( d_{111} = (2/3)^{1/2} D \). The arrows that are shown in Figure 1.11 are peak positions predicted from this equation using sphere sizes as determined from SEM; agreement with experimental data is quite good.

While this simple diffraction theory can predict the peak positions, it is unable to provide a quantitative explanation for any of the other features in the spectra. Recently, several groups have attempted to adapt the dynamical theory of x-ray diffraction to this purpose.\(^{47,48,50,84-86}\) However, this theory is based on the approximation that the refractive index contrast between the scattering centers and the interstitial medium is quite small, on the order of \( 10^-4 \), an approximation not valid for these silica-air crystals. For this reason, a detailed analysis of the shapes and intensities of the optical transmission function must rely on more complete treatments of scattering from periodic dielectrics. Theories of the optical properties of photonic band gap materials provide an avenue for this understanding; this issue has been explored more fully elsewhere.\(^{87}\)

An important feature of these spectra is the rising background that grows at shorter wavelengths; this causes the samples to look slightly hazy and could place limits on their use in many optical applications. This background has been observed, but rarely discussed, in gravity-sedimented crystals as well, and its origins remain obscure. While it does not clearly fit the \( \lambda^4 \) dependence expected for Rayleigh scattering, defects or sphere surface roughness could give rise to this phenomenon. Alternatively, it may represent the collective effect of diffraction off of all of the lattice planes other than the (111) planes.\(^{88}\)
If so, it is an intrinsic property of any periodic array of spheres, not merely of self-assembled colloidal crystals.

An interesting feature of the optical spectra is the increase in peak width as sample thickness is decreased. Typical normalized spectra are shown in Figures 1.12 and 1.16. As the thickness of the colloidal crystal increases, the optical transmission spectrum changes in characteristic ways. The spectral position of the stop band is reasonably well described by Bragg’s Law. The peak optical density grows monotonically with the number of layers. This increase is smooth and monotonic, and contains no evidence of a threshold thickness for the formation of a stop band.

In contrast, the width of the stop band displays a more dramatic dependence on film thickness. The observed narrowing of the stop band with increasing film thickness is reminiscent of the Debye-Scherrer effect in small crystallites. Here, the angular width of a diffraction line is limited by the highest spatial frequency accessible in the reciprocal lattice. The width is thus inversely proportional to the number of lattice planes, and arbitrarily narrow lines should be obtained by increasing the crystal thickness. However, in the colloidal crystals studied here, the narrowing of the stop band saturates above a certain critical thickness. Further increases in film thickness do not result in narrower band widths. Controlling and understanding this width is important in the design of optical elements using these materials, including filters, lasers, and all-optical switches. This result is summerized in Figure 1.17.
Figure 1.16. Normal-incidence optical density spectra for colloidal silica multilayers. These spectra are of three different films of 342 nm silica spheres, with (from top to bottom) 9, 25, and 50 layers. The solid curves are calculated using the scalar wave approximation. Both the data and the calculations have been scaled to uniform height and vertically offset for clarity. This overall multiplicative scaling is the only adjustable parameter in the calculation, since all other parameters (i.e., sphere diameter, material dielectric constants, number of layers) are determined by other
Figure 1.17. Experimental and calculated stop band widths as a function of the number of repeating layers of silica/air colloidal crystals, with a sphere diameter of 295 nm, and a dielectric contrast of $\psi_0 = 0.66$. The solid lines are calculated using the SWA, with no adjustable parameters.
These samples reach their limiting bandwidths at thicknesses of ~10 layers. We note that these limiting values correspond to fractional bandwidths of ~5%. This is typical of the widths observed in colloidal crystals, but is much broader than the widths encountered in other types of diffraction phenomena. For example, single crystal x-ray linewidths\textsuperscript{94} and reflection bandwidths of Bragg gratings in optical fibers\textsuperscript{95} can both be as narrow as 0.01% of their spectral position. One possible explanation for the broad widths observed here is that defects dominate the optical response, and prevent the observation of narrower natural linewidths. This seems unlikely, given the high sample quality. Alternatively, the bandwidth may be an intrinsic property of these strongly diffracting systems.

To evaluate this issue, a simple model is used to calculate transmission spectra. There has been extensive theoretical work in recent years on the description of the photonic properties of periodic dielectric media.\textsuperscript{16} One tractable analytic approach is the scalar wave approximation (SWA).\textsuperscript{96,97} Although this simple one-dimensional model has shortcomings,\textsuperscript{98,99} these difficulties are primarily related to its use in describing wave propagation along an arbitrary direction in the three-dimensional crystal. In the present work, we will be concerned solely with propagation along high symmetry directions of the crystal (i.e., the \{111\} axis). In this case, the one-dimensional SWA is appropriate. We note that an analytic expression for the stop band width can be derived from the SWA wave vector,\textsuperscript{100} but this only gives the limiting width for thick films. To obtain the dependence on thickness, one may calculate the optical spectra directly, and then extract the width numerically from these simulations.\textsuperscript{87}
The solid curves in Figures 1.16 and 1.17 represent the results of these calculations. Parameters used here include the sphere diameter and number of sample layers, both determined from SEM measurements, and the dielectric constant of the silica spheres, determined using index matching experiments as shown in Figure 1.18. In these experiments, the interstitial regions of a silica/air sample are filled with various fluids of known index; the peak optical density is smallest when the index of the fluid matches that of the spheres.¹⁰¹ For chemically prepared silica nanospheres, the refractive index is generally less than the index of bulk SiO₂.¹⁰² Here, index matching with isopropanol (n = 1.375) gave the smallest optical density. This value is used as the index of the spheres in the calculations presented here. The agreement between theory and experiment is remarkable, given that the SWA assumes an ideal, defect-free lattice.

These results suggest that the broad bandwidths observed in these samples are a fundamental property of close-packed spherical arrays. This may be understood as follows. For crystals of high dielectric contrast, diffraction is very strong, and the amplitude of the radiation attenuates rapidly with propagation distance into the crystal. As a result, most of the incident radiation interacts only with a few lattice planes, near the surface. The measured bandwidth is determined largely by these interactions near the input facet, and not by the subsequent propagation through the medium. Thus, increasing the thickness of the crystal above a certain critical thickness has little effect on the bandwidth.
Figure 1.18. The stop band width for a single 20-layer colloidal crystal of 353 nm silica spheres, as a function of dielectric contrast $\psi_0$. The data point on the far right ($\psi_0 \sim 0.66$) is the width measured on the sample as grown, with air in the interstitial regions. The remaining ten points are extracted from the transmission spectra when the interstitial regions are filled with various nonabsorbing dielectric liquids. The calculated result from the SWA is shown as a solid line.
Zacharaisen has given an expression for the critical thickness, derived within the framework of dynamical diffraction theory, however, this result is derived under the assumption of small dielectric contrast, and is therefore not valid for our systems. The dielectric contrast \( \psi_0 \) can be defined in terms of the average dielectric of the medium, \( \varepsilon_0 \), and the dielectric of the interstitial regions, \( \varepsilon_{\text{int}} \), according to \( \psi_0 = (\varepsilon_0 / \varepsilon_{\text{int}}) - 1 \). Here, \( \varepsilon_0 \) is given by a weighted average: \( \varepsilon_0 = \phi \varepsilon_{\text{sp}} + (1 - \phi) \varepsilon_{\text{int}} \), where \( \phi \) is the volume fraction occupied by the spheres. For close-packed spheres, \( \phi \approx 0.7405 \). Films such as the one shown in Figure 1.2 have a dielectric contrast of \( \psi_0 \approx 0.66 \). A more general result, valid for any \( \psi_0 \), can be found from the SWA, as follows. The critical thickness \( N_c \), expressed as the number of \{111\} layers, may be defined by \( |k_{\text{max}}| N_c d_{111} = 1 \), where \( k_{\text{max}} \) is the imaginary part of the photon wave vector at the center of the stop band and where \( d_{111} \) is the \{111\} lattice spacing. For close-packed spheres, \( N_c \) is given by:

\[
N_c = \frac{1}{\pi} \left( \sqrt{4 + \left( \frac{K \psi_0}{f + \psi_0} \right)^2} - 2 \right)^{-\frac{1}{2}}
\]

where \( K = (\beta/\beta') [\sin \beta - \beta \cos \beta] \), and where \( \beta = 2\pi \sqrt{3} / 8 \). For the silica/air films, \( N_c = 13 \) layers. A consequence of this analysis is that, for a crystal of a given thickness, the bandwidth should be a sensitive function of the dielectric contrast. As mentioned previously, one can control the contrast by filling the interstitial pores of a silica colloidal crystal with dielectric fluids. In this way, a range of different values of \( \psi_0 \) can be obtained for a single sample. As shown in Figure 1.18, the peak width narrows as the dielectric contrast decreases from either direction. The solid line is obtained from the SWA calculations as described above.
These results provide convincing evidence that broad stop band widths are intrinsic to these structures. Since the band width exhibits a dramatic change in behavior at the critical thickness while the peak attenuation does not, band width is evidently a more reasonable characterization of the importance of film thickness in these systems. This understanding of the nature of the stop band offers a prescription for engineering materials with narrower bandwidths. One must increase the number of layers and also decrease the diffraction efficiency per layer.

**Conclusions**

Materials whose dielectric constant varies spatially with sub-micron periodicity exhibit diffractive optical properties which are potentially valuable in a number of existing and emerging applications. In this chapter, such systems are fabricated by exploiting the spontaneous crystallization of monodisperse silica spheres into close-packed arrays. By relying on a vertical deposition technique to pack the spherical colloids into close-packed silica-air arrays, high quality samples can be prepared with thicknesses up to 50 microns. These samples are planar, and thus suitable for optical characterization. Scanning electron microscopy (SEM) of these materials illustrates the close-packed ordering of the spherical colloids in planes parallel to the substrate; cross-sectional SEM micrographs of the arrays as well as optical methods are used to measure sample thickness and uniformity. Normal-incidence transmission spectra in the visible and near-infrared show distinct peaks due to diffraction from the colloidal layers. While these basic optical characteristics are similar to thicker and polycrystalline gravity-sedimented colloidal crystals, the systematic control over the number of colloidal layers
allows the effect of sample thickness on the optical spectrum to be studied for the first time. We found that the stop band width and peak attenuation depend on the number of layers and on the dielectric contrast between the spheres and the interstitial regions, both of which are experimentally controlled. The results are in good agreement with the predictions of the scalar wave approximation.
References


Chapter 2

The Fabrication and Photonic Band Gap Engineering of

Photonic Multilayers

Introduction

Traditional colloidal crystals are three dimensional periodic structures formed from monodisperse colloids.\(^1-3\) Because of their diffractive optical properties they are a type of photonic crystal\(^4-6\) and may have applications as optical filters and switches,\(^7-9\) high density magnetic data storage devices,\(^10\) chemical and biochemical sensors,\(^11,12\) or as removable scaffolds for the formation of highly ordered, macroporous materials.\(^13-22\) They are also useful as model systems for fundamental studies of crystal melting and phase transition behavior.\(^23-26\) The process of colloidal crystallization has been extensively studied, leading to the development of several methods to make high quality colloidal crystals with few crystalline defects. These techniques include electrostatically induced crystallization,\(^8,27-30\) gravity sedimentation,\(^1,24,31-34\) electrohydrodynamic deposition,\(^35-37\) colloidal epitaxy,\(^38,39\) physical confinement\(^3,40\) and convective self-assembly.\(^41,42\) Bimodal AB\(_2\) and AB\(_{13}\) colloidal crystals with complex structures have also been observed in binary mixtures of hard-sphere colloids with specific radii ratios.\(^43-45\) In this chapter a method to make a new form of colloidal crystal, a multilayer crystal, using successive deposition of crystals of colloids of arbitrary sizes is described.
Experimental Section

Materials and Substrates. All solvents and chemicals are of reagent quality and used without further purification except for tetraethoxysilane (99%, Alfa) which is freshly vacuum distilled before use. 200 proof ethanol is obtained from Pharmaco Products and 29.6% ammonium hydroxide is purchased from Fisher. Ultrapure water (18.2 MΩcm⁻¹) is used directly from a Milli-Q water system. Styrene is obtained from Acros. 2,2-Diethoxyacetophenone (Aldrich, 95%) is used as UV photoinitiator. Microslides (75 × 25 × 1 mm, Fisher) are cut into two equal halves along the long sides and are used as substrates. Glass scintillation vials (20 mL, Fisher) are used as experimental cells.

Instrumentation. Scanning electron microscopy is carried out on a Philips XL30 ESEM. A CrC-100 sputtering system is used to sputter a thin layer (3–4 nm) of gold on samples before SEM analysis. An Oriel model 60000 UV lamp (320 W) with 68806 basic power supply is used to initiate the polymerization of styrene. Transmission spectra are obtained using an Ocean Optics ST2000 fiber optic ultraviolet-visible-near-infrared spectrometer.

Monodisperse Silica Colloids Synthesis and Purification. Monodisperse SiO₂ nanospheres are synthesized following the Stober-Fink-Bohn method by the hydrolysis and condensation of tetraethoxysilane (TEOS) in the presence of water and ammonia.46 Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviation smaller than 7% are obtained through strict control of the reaction conditions.47 All the solvent (200 proof ethanol) and reagents (water and 29.6% ammonia) except for TEOS which is vacuum distilled prior to use, are filtered through 0.2 μm syringe filters (Gelman
Sciences). More details of the synthesis process are described in Chapter 1. The synthesized silica alcosols are purified by repeated centrifugation and ultrasonic dispersion cycles in order to remove impurities times and the resulting silica alcosols can be stored in sealed Erlenmeyer flasks for years. The sizes and size distributions of these samples are obtained from SEM measurement. Over 200 spheres are sized using SEM in order to arrive at the reported diameters.

**Experimental Apparatus and Procedures.** Prior to use all microslides and scintillation vials are soaked in chromic-sulfuric acid clearing solution overnight, rinsed well with ultrapure water from Milli-Q water system, and dried in a stream of nitrogen. A clean microslide is then placed into 15 mL of purified silica alcosol in a clean scintillation vial. The vial is covered by a 1200 mL crystallizing dish to keep out external airflow and contamination. The entire apparatus is placed on a vibration-free bench in a temperature-controlled laboratory (22°C, ± 1°C). The whole experimental apparatus is shown in Figure 1.1. For the preparation of these multilayer samples no substrate withdrawal is necessary.

The volume fractions of different samples are determined by drying 6 mL purified silica alcosol in 80°C vacuum oven overnight and then weighing the residual solid. 2.04 g/mL is used as the density of silica, though its actual density may be somewhat lower. Then, the samples are diluted or concentrated using a centrifuge-redisperse cycle to the required volume fractions.

The photonic multilayer samples are fabricated by successive dip coating. After each single coating is deposited, the film is air-dried for at least 24 hours and dipped again into another purified silica alcosol with different particle size. The coating and
drying cycle can be repeated to create photonic multilayer samples with arbitrary order of different sphere sizes.

**Preparation of Three-Dimensionally Ordered Macroporous Polystyrene Films Using Silica Multilayer Colloidal Crystals as Templates.** A schematic outline of the procedure for producing three-dimensionally ordered nonconductive macroporous polymers is shown in Figure 2.1. The microslide with SiO₂ colloidal crystal on its surface

![Schematic diagram](image)

**Figure 2.1.** A schematic outline of the procedure for making macroporous polymers.

is covered by another microslide and dipped in 1-2 ml of a monomer (styrene with 1% (weight%) photoinitiator 2,2-dithoxyacetophenone). Capillary forces draw the liquid monomer into the void spaces between the silica particles. It takes several seconds for the monomer to completely fill the cell. Due to refractive index matching between silica
and monomer, the cell becomes transparent. The styrene is then cross-linked by exposure to UV light for 30 hours. Afterwards one or both microslides are carefully removed and the freestanding polymer film is soaked in 4% hydrofluoric acid solution (about 15 ml) overnight to remove the silica. The resulting macroporous polymer is washed with Milli-Q water and air-dried. To form a stronger self-standing macroporous polymer, a 0.1 mm Teflon spacer can be used to separate the two microslides. The films exhibit striking iridescence due to Bragg diffraction of visible light by the ordered air spheres in the polymer.

**Characterization of the Photonic Silica Multilayer Colloidal Crystals and Macroporous Polystyrene Films.** The silica colloidal crystals and macroporous polymers can be affixed to conductive carbon tape and prepared for scanning electron microscopy by sputtering a thin layer (3-4 nm) of gold onto the surface. A Philips XL30 ESEM has been used to evaluate the samples. The samples are broken using a sharp razor blade and are tilted 30-40° to obtain the cross-sectional images.

The optical properties of the silica colloidal crystals and templated macroporous polystyrene films are evaluated by measuring their transmission spectra at normal incidence, using an Ocean Optics ST2000 fiber optic spectrometer. Clean glass microslides and pure polystyrene films are used as references.

**Results and Discussions**

The multilayer colloidal crystal is schematically represented in Figure 2.2A. Balls of different colors represent submicron silica colloids of different sizes. Each layer of the crystal is a close-packed array of colloids, and the overall structure consists of
successively stacked crystals, formed from colloids of arbitrary diameters. To make these structures, we first coat a glass slide using ~15 ml of a monodisperse silica sol (1% particle volume fraction). After ethanol slowly evaporates over 3-5 days, a large area (1 cm × 3 cm), iridescent colloidal crystal film is formed on the glass slide. The film is drawn out of the silica sol and air-dried, then immersed into ~13 ml of another silica sol with a different particle size. This coating-drying-coating cycle can be repeated up to ten times and the resulting colloidal crystal films retain their high crystalline quality. In this way, a layered structure with an arbitrary pattern of sphere sizes can be assembled.

The high uniformity of the resulting crystals can be illustrated by the transmission (Figure 2.2B) and reflection (Figure 2.2C and 2.2D from different angles) photographs of

![Figure 2.2](image.png)

**Figure 2.2.** (A) A schematic outline showing a “superlattice” colloidal crystal made by consecutive deposition of colloidal multilayers from colloids of three different sizes. Photographs showing the colors transmitted (B) and reflected (C and D, from different angles) from a crystal made by successive coating of 430, 253 and 338 nm silica colloidal multilayers. The top part of the sample shows the single coated area (430 nm), the middle part shows the double coated area (253 nm multilayers on top of 430 nm one) and the bottom part shows the triple coated area (430, 253 and 338 nm multilayers).
a sample three-layer crystal. This example is formed by consecutive deposition of 13 layers of 430 nm silica spheres, followed by 16 layers of 253 nm silica spheres, followed by 10 layers of 338 nm silica spheres. We describe the multilayer colloidal crystal pattern by listing the sphere size from bottom to top. For example, the sample in Figure 2.2 is referred to as 430 nm/253 nm/338 nm. The reflected colors are caused by Bragg diffraction of visible light by the three-dimensionally ordered arrays of submicron colloids. When two overlapping layers are made from colloids with extremely different sizes, most of the reflected light from the bottom layer will transmit through the upper layer, resulting in the transparent appearance of the second layer in Figure 2.2C (430 nm/253 nm).

Crystalline quality is among the most important parameters in determining the performance of colloidal crystals in optical applications. Figure 2.3 shows the typical top-view and cross-section SEM images of each "step" of the sample shown in Figure 2.2. In Figure 2.3A, the hexagonal close-packed arrangement of the top 430 nm layer is evident. The sharp peaks in the two-dimensional fast Fourier transform (FFT, inset) of a low-magnification image confirm the presence of long-range crystalline order extending over the largest length scales (40 × 40 μm²) accessible in a single image. The stacking of close-packed layers shown in Figure 2.3B demonstrates the high degree of order along the (111) crystallographic axis, perpendicular to the substrate. The long-range order of the second and the third "steps" of this stacked crystal is confirmed by the top-view SEM images and FFTs shown in Figure 2.3C and 2.3E. This ordering extends over the whole area of each multilayer, as demonstrated by the uniform visual appearance of the samples (see Figure 2.2). Figure 2.3D and 2.3F clearly show the overlapping of close-packed
multilayers with different sphere sizes. Each layer is highly ordered and remains oriented with its (111) axis parallel to the slide.

Though images such as these confirm a regular close-packed arrangement, it is difficult to distinguish between the fcc (ABCABC...) and hcp (ABABAB...) structures.

Figure 2.3. Typical scanning electron microscopy (SEM) images showing top and side views of each multilayers of a “superlattice” colloidal crystal made by consecutive deposition of silica colloidal multilayers with three different sizes. (A) and (B) show the single coated area (430 nm silica multilayers). (C) and (D) reveal the double coated area (253 nm multilayers on top of 430 nm multilayers). (E) and (F) show the triple coated area (430 nm, 253 nm and 338 nm silica multilayers from bottom to top). The insets of (A), (C) and (E) show Fourier transforms (FFT) of 40 × 40 µm².
even for each individual multilayer. Theoretical calculations, though, have indicated that fcc structure is stabilized slightly.\textsuperscript{48} Also, it is important to note that these crystals are not perfect; defects such as cracks and point defects are observed. However, there are apparently no grain boundaries over areas as large as 1 cm\textsuperscript{2}, and the (111) axis is oriented perpendicular to the underlying substrate.\textsuperscript{41}

An important feature of the convective assembly process is that it permits control over the thickness of the resulting crystals. The number of colloid layers deposited, $k$, is related to the particle volume fraction and sphere size, according to:\textsuperscript{41,49}

$$k = \frac{\beta L \varphi}{0.605 d (1 - \varphi)}$$

where $L$ is the meniscus height, $\beta$ is the ratio between the velocity of a particle in solution and the fluid velocity and is taken to be 1, $d$ is the particle diameter, and $\varphi$ is the particle volume fraction in solution. This precise control is one factor which permits the photonic band gap behavior to be tuned in the multilayered crystals.\textsuperscript{50}

Since the multilayer colloidal crystals are stacks of colloidal crystals with different particle sizes, the interfacial packing is an important characteristic of these samples. There are essentially two types of stacking: big spheres on smaller ones and small spheres on bigger ones. We have tested a large number of combinations using colloids from 200 nm to 500 nm and found that there is no significant difference in the visual appearance or transmission spectra of the resulting multilayer crystals. Figure 2.4 shows SEM images of two stages in the crystallization process of big silica spheres (338 nm) on a layer of smaller spheres (253 nm). A hexagonal close-packed monolayer is formed at the immediate crystalline growth front (Figure 2.4A), while a three monolayer
crystal is formed at 20 µm from the growth front (Figure 2.4B). Further SEM observation shows the thickness is uniform starting at about 100 µm from the growth front (Figure 2.3F). This gradient film thickness has been observed in our previous work, and can be

**Figure 2.4.** Typical SEM images reveal the interfacial stacking of 338 nm silica on a double coated silica colloidal crystal (253 nm multilayers on top of 430 nm one). (A) Monolayer packing at the immediate crystal growth front. (B) Three layers packing at the region 20 µm from the crystal growth front.
explained by the thinning of the meniscus at the immediate crystalline growth front.\textsuperscript{41} From the above observations, we conclude that larger silica spheres crystallize on a layer of smaller ones just as they do on a flat surface. This is easily understood, especially for spheres with significant differences in their diameters, since the curvature of the big spheres is larger than that of the interstitial spaces formed by the close-packing of smaller spheres.

For the spheres with similar sizes, we observed some unusual packing at the interface between the layers, reminiscent of packing seen with template-directed colloidal crystallization.\textsuperscript{38} In our case, however, the (111) plane instead of (110) plane acts as the template for crystallization. For the case of small spheres stacked on bigger ones, the crystallization process is complex since the curvature of the interstitial spaces formed by the hexagonal close-packing of big spheres is larger than the diameter of the smaller spheres. For this reason, the smaller spheres can be trapped in the interstitial spaces at the interface between layers. Obtaining clear views of these interfaces without disrupting their structure is difficult, however. We solve this problem using macroporous polymers formed from the multilayer samples. These are faithful replicas of the starting silica multilayer colloidal crystals, and are much easier to cleave in order to image the interfaces, as shown in Figure 2.5.

Figure 2.5A shows a two-layer macroporous polystyrene multilayer, composed of a crystalline array of spherical voids of 253 nm diameter, on top of a crystalline array of 430 nm voids; Figure 2.5B shows a three-layer macroporous polymer (338 nm/430 nm/253 nm). The inset in Figure 2.5A shows a high-magnification SEM image which reveals the interface between the array of 253 nm voids and the array of 430 nm voids.
Figure 2.5. Typical cross-sectional SEMs of macroporous polystyrene films templated from the multilayer silica colloidal crystals. (A) A two multilayers sample composed of 253 nm voids on top of 430 nm voids. The higher magnification image in the inset shows the interfacial stacking. (B) A three multilayers sample composed of 338 nm, 430 nm and 253 nm voids stacked from bottom to top.
The flat, close-packed arrangement of the smaller voids is clearly seen. Since the voids are an exact replication of the silica colloids used as a template in the formation of this macroporous polymer sample, the ordering of the air voids represents that of the original silica colloids. From these images, we conclude that the smaller spheres assemble as if the underlying array of bigger spheres presented a flat surface during the crystallization process. Given the aforementioned considerations, this result is somewhat surprising. Further studies using confocal microscopy may be useful for understanding this observation. However, from a practical standpoint, this result implies that particle sizes for each sub-component of the colloidal multilayer crystal can be arbitrarily selected, at least within the range of colloid diameters studied to date.

Figure 2.6 shows the optical transmission spectra for two three-layer silica multilayer colloidal crystals, where the three layers have been deposited in two different orderings. The blue lines represent spectra from each individual layer, while the red lines show the doubly overlapped multilayers and the green lines represent the triply overlapped multilayers. In the latter two cases, we compare doubly overlapped and triply overlapped samples with different layer orderings. The peaks around 570 nm, 764 nm and 965 nm arise from the Bragg diffraction of incident light within each layer, as seen in the blue curves. The peak positions can be related to the sphere diameter and the effective refractive index of the medium using Bragg's law, \( \lambda_{\text{max}} = 2n_{\text{eff}}d_{111} \), where \( d_{111} \) is the (111) lattice spacing. We have also observed an intense secondary diffraction peak from the 430 nm crystalline arrays near 520 nm. Both the large amplitude and the position of this peak are consistent with the results from previous studies of crystalline colloidal arrays. We note that the spectra of the multilayer colloidal crystals have
Figure 2.6. Normal incidence transmission spectra of two silica “superlattice” colloidal crystals. These curves have been vertically offset for clarity. (A) Single coated area (253 nm multilayers, black line), double coated area (430 nm multilayers on top of 253 nm one, red line) and triple coated area (253 nm, 430 nm and 338 nm multilayers from bottom to top, green line) as schematically outlined by the inset. The dotted blue line shows a reference spectrum of 338 nm silica colloidal crystal with the same thickness as the 338 nm multilayers of above sample. (B) Same as (A) except for the inverse order of the first two multilayers (253 nm on top of 430 nm multilayers) as revealed by the inset.
features which correspond to peaks in each of the spectra of the crystals with only one size of colloid. This correspondence confirms the high crystalline quality of each multilayer of the composite sample, and also suggests that the optical properties of the composite multilayers can be approximated from the spectra of the individual layers by a simple superposition. The similarity of the spectra for the doubly and triply overlapped regions with different layer ordering (red and green lines in Figure 2.6) provides additional evidence that the interfaces do not play a significant role in the overall optical properties.

We also note that the overlapping of the secondary diffraction peak from the 430 nm colloidal layer with the 570 nm peak from the 253 nm colloidal layer produces a single, broader peak. This suggests one way to tailor the photonic band gap properties of the multilayer colloidal crystal. To create a broader stop band, crystals of spheres with similar sizes can be combined, producing a composite film which inhibits light propagation over a wider range of wavelengths, and presumably a wider range of angles as well. To explore this idea further, we have produced a sample consisting of three layers of crystals composed of spheres of similar sizes. Figure 2.7A shows the transmission spectrum of a 303 nm/325 nm/338 nm sample. The green, black and red lines represent reference transmission spectra from each individual crystal. For these non-overlapped samples, the thickness of each of the crystals is the same as it is in the composite multilayer sample. We observe significant broadening of the relative width \((\Delta \lambda/\lambda)\) of the stop band in the (111) direction, from \(\sim 6-7\%\) for the single crystals to \(\sim 10\%\) for the multilayer sample. Figure 2.7B shows the relative insensitivity of this broader stop band to the angle of incidence of the radiation. This result suggests that by
overlapping many colloidal crystals with similar sphere sizes the effective band width can be increased; this may be a viable strategy for creating lightweight and large area optical filters.

In order to evaluate whether the optical spectrum of a multilayer colloidal crystal is determined simply by superposition of the spectra of its component crystals, we show the sum of the spectra of the individual layers in Figure 2.7A (dashed curve) compared to the measured spectrum of the multilayer film. Interestingly, the spectrum of the tri-layer crystal is similar to, but not identical to, the sum of the spectra of the three individual layers. New and fairly narrow spectral features are formed, presumably as a result of coherent interference effects between the stop bands of the three sub-units. These features are reminiscent of “minibands,” similar to the effects seen in electronic superlattices, and their presence suggests the possibility of tailoring mid-gap resonances in photonic crystals. The study of such features is of ongoing interest.52
Figure 2.7. (A) Normal incidence transmission spectra of a 338 nm/325 nm/303 nm silica "superlattice" colloidal crystal (blue line). The black, red and green lines show the spectra of reference silica multilayers of 338 nm, 325 nm and 303 nm with same thickness as each multilayers of above sample. The dotted black line shows the additive spectrum of above three reference spectra. (B) Optical transmission spectra reveal the angular dependence of above "superlattice" sample.
Conclusions

In this chapter, an efficient method to fabricate colloidal crystals with multilayer structures from a variety of colloids with different sizes is described. These materials exhibit approximately additive photonic band gap properties, which can be tailored by manipulating secondary diffraction, film composition and sphere size. Although only silica multilayer colloidal crystals have been shown here, we found this method can be easily extended to other monodisperse colloids, such as polystyrene beads. By alternating deposition of silica and polystyrene layers, a one-dimensional photonic crystal with three-dimensional sub-structure could be made. Such a geometry is similar to Rugate filters and may find important application in interference coating. Other non-optical applications can also be envisioned, such as the use of size-gradient macroporous polymers in membrane separations. Finally, it should be possible to form a multilayer consisting of many alternating layers of two different sphere sizes. In this geometry, it would be possible to form true “superlattice” photonic crystals with strong interactions between waves diffracted over large distances. The optical properties of such systems would present an entirely different way of tailoring the photonic properties of these colloidal crystal films.
References


Chapter 3

Template-Directed Preparation of Macroporous Polymers with Oriented and Crystalline Arrays of Voids

Introduction

Macroporous materials, those with pore diameters greater than 50 nanometers,\textsuperscript{1} have a wide range of applications in chemistry. Macroporous polymers, in particular, can be used as catalytic surfaces and supports,\textsuperscript{2,3} separation and adsorbent media,\textsuperscript{4-6} biomaterials,\textsuperscript{7-10} chromatographic materials,\textsuperscript{11-13} and thermal, acoustic or electrical insulators.\textsuperscript{14-17} In nearly every case, the utility of the porous system is a sensitive function of the internal pore diameters, their distribution,\textsuperscript{18-21} and their morphology.\textsuperscript{11} As a result, most of the synthetic approaches to creating these materials, both polymeric and inorganic, have focused on creating internal voids with monodisperse and controllable diameters.\textsuperscript{1,22,23} Towards this end, this chapter describes a templating strategy for fabricating such materials, with voids ranging from 50 to 500 nanometers in diameter.

The motivation in this work is the growth of samples suitable for optical characterization. The materials described below are arrays of spherical air voids embedded in a host polymer matrix, exhibiting crystalline order over length scales as long as 1 cm. Since the voids have diameters of \(~0.5\,\mu\text{m}\), the structure acts as a diffractive optic for visible light. Recently, these diffractive properties have received
considerable attention, since theoretical modeling of photonic behavior has illustrated that control over the symmetry and the host matrix allow very strong and specific optical properties to be engineered.\textsuperscript{24-28} Numerous optical applications have been proposed for materials exhibiting long-range three-dimensional dielectric periodicity, including for the control of spontaneous emission rates,\textsuperscript{29-32} substrates for planar waveguides,\textsuperscript{33} infrared filters\textsuperscript{34} linear and nonlinear optics and chemical sensors.\textsuperscript{35-37} In most of these examples the materials are diffractive only in the infrared and microwave region because of the limitations of lithographic processing. In contrast, chemically prepared macroporous materials have no intrinsic limit on the size of the pores, and thus offer a route to creating photonic materials operating at visible, ultraviolet and even soft x-ray wavelengths. However, in order to be useful in optical technologies, an ordered macroporous sample must meet a number of stringent material requirements. The sample must be of high optical quality (no cracks or bubbles), cast as a film of controlled thickness on an optical substrate, and uniform over a square centimeter or more.

A number of techniques have been developed for the fabrication of well-controlled macroporous polymer materials suitable for non-optical applications. These include ion-track etched polymers,\textsuperscript{38} chemically induced phase separation,\textsuperscript{39,40} self-assembly of block copolymers\textsuperscript{21} and copolymerization methods.\textsuperscript{41-44} While these methods do lead to the formation of high quality macroporous polymers, they do not provide the long range crystalline order and sample format required for optical applications. For these requirements, methods that rely on the self-assembly of a sacrificial template to define the porous structure are more suitable. Work in the last few years has demonstrated the utility of self-organizing systems as templates for the growth
of a second material. These include surfactants,45 biological systems,46 liquid-droplet surfaces,47 and emulsions.18,19 Many of these systems are capable of producing macroporous materials of both polymers and inorganic oxides with pore sizes \( \geq 50 \) nm.18,19,46,48,49 However, in these instances the templates are polycrystalline, and the resulting samples lack the long range order and uniformity necessary for optical characterization.

A more suitable template for the production of optical materials is an array of polymer or silica spheres which, even before templating, exhibits diffractive properties. This has been demonstrated recently by several examples in which thick gravity-sedimented colloidal crystals or thin colloidal monolayers served as scaffolds for the production of inorganic macroporous materials.1,23,50-69 In a few instances, the samples were of high enough quality to obtain diffractive optical data which resulted from the crystallinity of the porous structure.1 Extending this method to the production of polymeric systems has also been recently reported.22,52,70 For example, Xia et al. used latex spheres as templates for forming ultrathin (d < 5 microns) three-dimensional macroporous poly(urethane) membranes.22,70,71 Though no optical characterization was reported, this result demonstrates the potential of using colloids in template-directed syntheses, especially of macroporous polymers.

This chapter describes a versatile templating strategy for creating macroporous polymer films appropriate for quantitative comparison with standard models of diffractive optics. We chose to work with polymers, rather than inorganic matrices, because such materials may extend the use of diffractive optics into applications that require lightweight and/or low-cost materials.72-76 In addition, the polymer curing
process involves much less volume shrinkage than the corresponding precursor decomposition used to make inorganic systems. This allows for the formation of large area (≈1 cm²) samples which can be cast as films on optical substrates. Finally, although polymeric refractive indices are lower than those of many inorganic materials, an ordered lattice of air-spheres in a polymer is predicted to exhibit photonic band gap behavior, albeit over a smaller range of wavelengths and incident angles than the corresponding inorganic film. Even a partial band gap, such as the one predicted by theory for these materials, is a useful property in numerous linear optical applications ranging from wavelength rejection filters to optics for distributed feedback lasers.

The macroporous polymer films in this work are formed around silica colloidal crystal templates, which are themselves designed for optical applications. These templates were grown following a method that casts colloidal films with controlled thickness in planar formats as described in detail in Chapter 1. The use of these high quality templates ensures that the resulting polymer films meet the specifications for optical characterization. This strategy also relies on the use of silica, not latex, spheres as a template. This makes it possible to remove the template at room temperature by treatment with dilute hydrofluoric acid. Thus, macroporous films of a wide variety of polymers can be cast through either photo-initiated or thermally initiated polymerization. Visualization of the macroporous polymers using scanning electron microscopy (SEM) reveals that the samples exhibit not only an ordered void structure from the silica spheres, but also a uniform distribution of pores which form around points where the spheres once touched. The sizes of these small pores are a sensitive function of monomer viscosity. They may be of utility in other non-optical applications, such as size selective filtration.
or electrophoresis. Optical transmission studies of the polymer/air-sphere materials illustrate the existence of a optical stop band, in which strong diffraction effects limit the optical transmission of the film. These transmission spectra are consistent with calculations based on the scalar wave approximation.\textsuperscript{82,83}

**Experimental Section**

**Materials and Substrates.** All solvents and chemicals are of reagent quality and are used without further purification except for tetraethoxysilane (Alfa, 99%) which is freshly vacuum distilled before use. 200 proof ethanol is obtained from Pharmaco Products. 29.6% ammonium hydroxide and 49% hydrofluoric acid are obtained from Fisher. Ultra-pure water (18.2 M\(\Omega\)cm\(^{-1}\)) is obtained from a Millipore Ultra-pure Water System. Commercially available monomers are used: methyl methacrylate (Aldrich), methyl acrylate (Aldrich), ethyl acrylate (Aldrich), butyl acrylate (Aldrich), styrene (Acros), NOA 60 (polyurethane, Norland), F113 (epoxy, Tra-Con), epoxy resin (Hardman), aniline (Fisher) and p-xylylenebis(tetrahydrothiophenium chloride) (Aldrich). 2,2-Diethoxyacetophenone (Aldrich, 95%) is used as UV photoinitiator. Commercially available polystyrene (average \(M_w\) \(\sim\)230,000, melt index 8.5, glass transition temperature \(T_g\) 94°C) and PMMA (average \(M_w\) \(\sim\)350,000, glass transition temperature \(T_g\) 122°C) are obtained from Aldrich. The refractive indices of the resultant polymers are: PMMA (1.49),\textsuperscript{84} PMA (1.472–1.480),\textsuperscript{84} polystyrene (1.59–1.592),\textsuperscript{84} polyurethane (1.5–1.6),\textsuperscript{84} and epoxy (1.55–1.60).\textsuperscript{84} 20 ml scintillation vials and glass microslides (75\times25\times1 mm) are obtained from Fisher and cleaned in a chromic-sulfuric acid cleaning solution (Fisher)
overnight, rinsed with Milli-Q water (18.2 MΩcm⁻¹), and dried in a stream of nitrogen. 0.1 mm Teflon spacers are obtained from Aldrich.

**Instrumentation.** Scanning electron microscopy and EDAX are carried out on a Philips XL30 ESEM. Transmission spectra are obtained by using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer. An Oriel model 60000 UV lamp (320 W) with 68806 basic power supply is used to initiate the polymerization. A Fisher Isotemp 2150 circulator and an acrylic open bath are used to control the polymerization temperature to ± 0.5°C accuracy. A CrC-100 sputtering system has been used to sputter a thin layer (3-4 nm) of gold on the samples before SEM analysis.

**Colloidal Silica Synthesis and Colloidal Crystal Growth.** Monodisperse SiO₂ nanospheres are synthesized following the Stober-Fink-Bohn method. Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviation smaller than 5% are obtained through strict control of the reaction conditions. The experimental section of chapter 1 gives the detailed synthesis of silica nanospheres and their subsequent purification. The sizes and size distributions of these samples are obtained from SEM measurements. The methods described in the experimental section of chapter 1 and our previous paper are used to fabricate three-dimensionally ordered planar colloidal crystals with thickness ranging from one monolayer to 50 μm. Through convective self-assembly, an iridescent colloidal single crystal grows on the surface within 3-4 days while ethanol evaporates. Typically films of 10-50 layers can be prepared in a single coating, while successive coats can make films up to 200 layers (about 50 μm depending on sphere size) (see Figure 3.1). These materials were used as templates for preparing macroporous polymers.
Figure 3.1. Typical scanning electron micrograph (SEM) images of a SiO$_2$ colloidal single crystal template (298.6 nm) for fabricating macroporous polymers. (A) Top view (×30,000) with inset showing the FFT of a low magnification image of a 40 × 40 μm$^2$ region. (B) Side view (×6,000) of the same sample, from which the film thickness can be determined.
Fabrication of Three-Dimensionally Ordered Nonconductive Macroporous Polymers. A schematic outline of the procedure for producing three-dimensionally ordered nonconductive macroporous polymers is shown in Figure 3.2. The microslide with SiO₂ colloidal crystal on its surface is covered by another microslide and dipped in 1-2 ml of a monomer. For photoinitiated monomers, such as styrene and methyl methacrylate, 1% (weight%) photoinitiator is added prior to the photo-polymerization. Capillary forces draw the liquid monomer into the void spaces between the silica particles. Filling times range from several seconds for a low viscosity precursor such as styrene to 5-10 minutes for a high viscosity monomer such as NOA 60. Due to refractive index matching between silica and monomer, the cell becomes transparent. The prepolymer solutions are then cross-linked thermally at 60°C (for F113 and Hardman epoxies) or by exposure to UV light (for acrylates and styrenes) for several hours. The polymerization time depends on the monomers. Urethanes will be polymerized in minutes, while styrene can take days. Afterwards one or both microslides are carefully removed and the freestanding polymer film is soaked in 4% (v/v) hydrofluoric acid solution (about 15 ml) overnight to remove the SiO₂. The resulting macroporous polymer is washed with Milli-Q water and air-dried. Depending on the properties of different polymers, the products can be rigid (poly(methyl methacrylate) and poly(styrene)) or flexible (poly(urethane)). To form a stronger freestanding macroporous polymer, a 0.1 mm Teflon spacer can be used to separate the two microslides. The films exhibit striking iridescence due to Bragg diffraction of visible light by the ordered air spheres in the polymer. The sizes of the spherical pores and the thickness of the macroporous polymer can be controlled by changing the thickness and sphere size of the template silica film.
Fabrication of Three-Dimensionally Ordered Nonconductive Macroporous Polymers from Commercially Available Polymers. Due to the long polymerization time of monomers, especially for styrenes and acrylates, and the requirement of special instruments such as the UV lamp, photopolymerization is problematic for fabricating macroporous polymers in large scales. To overcome this problem, we have also used commercially available polymers as fillers. When the polymers are heated above their glass transition temperatures ($T_g$), they become viscous liquids and can penetrate into the voids between the templates' spheres. The microslide with SiO$_2$ colloidal crystal on its surface is surrounded and glued to another four microslides using photopolymerizable urethane (NOA 60) to make a container. Then 1-2 grams of commercial available
polymers (powders or pellets) are put into the container. The container is then put into an oven at a temperature 20-30°C higher than the glass transition temperature of the polymer. After the voids are filled with polymer, the colloidal crystal becomes transparent due to refractive index matching between silica and polymer. Then the container is cooled down to room temperature and the templating silica is removed using 4% HF. The resulting macroporous polymer is washed with Milli-Q water and air-dried. The thick macroporous polymer films exhibit striking iridescence due to Bragg diffraction of visible light by the ordered air spheres in the polymer.

Fabrication of Macroporous Conductive Poly(p-phenylenevinylene) (PPV).

The PPV precursor is prepared according to the method described before.95 We choose to use the tetrahydrothiophenium (THT) derivative of the monomer since it can be obtained in 90% purity from Aldrich. In addition, the THT leaving group is quite stable and promotes higher reaction yields and longer polymer chain. The insoluble impurities can be removed by filtration of an aqueous solution of monomer. 7 grams of the purified monomer are dissolved in 200 mL of Milli-Q water giving a 0.1 M monomer solution which should be cooled to 0°C and flushed with argon in a three necked flask. Polymerization proceeds by adding 200 mL of a 0.08 M NaOH solution also cooled to 0°C and flushed with argon. After the addition of base, the reaction solution will become viscous within 30 minutes. During this time, care should be taken to keep the entire reaction at 0°C. To stop the reaction, excess base must be neutralized by the addition of acid. Normally, 10-20 mL of 1 M HCl are required to bring the pH down to 7. Once neutralized, the solution can be transferred to dialysis tubing (Spectra-Por #3, MWCO: 3,500) and dialyzed in Milli-Q water in the dark for several days. In order to recover a
solid product of precursor PPV it is necessary to remove the excess water. Dialysis of the solution against isopropanol is the best way to extract the water. After the dialysis is complete, the same bags are transferred into a refrigerated container of 300 mL of isopropanol containing a molecular sieve capable of sorbing the excess water. After several changes of the isopropanol solution over several days, the bags will shrink leaving a milky white solution or pale yellow solid adhered strongly to the inside of the bag. Since the product cannot be scraped out of the tubing it must be immediately dissolved in methanol by rinsing the bags with 100 mL of methanol. Normally, the resulting methanol solution is pale yellow and slightly viscous.

A schematic outline of the procedure for producing three-dimensionally ordered macroporous PPV is shown in Figure 3.3. The microslide with SiO$_2$ colloidal crystal on its surface is laid down on the flat bottom of a polystyrene dish. Then 50 mL of PPV precursor methanol solution is poured into the polystyrene dish. Once the methanol has evaporated in about 2 days, the PPV precursor which interpenetrates the template pores can be reacted. To remove the overcoated PPV precursor on top of the colloidal crystal, the microslide is broken carefully along a precut line on the opposite side of the colloidal crystal and the overcoated PPV precursor film can be easily peeled off. The microslide is then heated to 250°C for 30 minutes under vacuum to form fully conjugated PPV as shown in equation [1]:

\[
\begin{align*}
\text{PPV} & \xrightarrow{\text{Vacuum elimination } T = 250^\circ \text{C}} \quad \text{Cast film} \\
& \xrightarrow{- \text{(CH$_3$)$_2$S}} \quad \xrightarrow{- \text{THT}} \\
& \xrightarrow{\text{II} \quad \text{Precursor Polymer Film}} 
\end{align*}
\]
Afterwards the microslide is soaked in 4% hydrofluoric acid solution (15 mL) overnight to remove the silica template. The resulting macroporous polymer is washed by Milli-Q water and air-dried. The macroporous PPV samples are flexible and exhibit striking iridescence when dipped in water.

![Diagram showing the process of dip coating and etching to create macroporous PPV](image)

**Figure 3.3.** A schematic outline of the procedure for making macroporous PPV.

**Fabrication of Macroporous Conductive Poly(aniline) (PAN) by Electrochemical Synthesis.** A schematic outline of the procedure for producing three-dimensionally ordered macroporous poly(aniline) is shown in Figure 3.4. The silica colloidal crystals are grown in an analogous manner as in Chapter 1 except for using ITO (indium tin oxide) coated glass plates instead of plain glass microslides as the substrates. The ITO-glass with SiO<sub>2</sub> colloidal crystal on its surface is dipped in 25 mL of 3 M HCl solution and 3 mL of aniline. Then a copper wire that is bent in a "U" shape at one end is dipped into the solution. The circuit construction for polyaniline electrochemical synthesis is shown in Figure 2. Then a potential of 1.3 V is applied to the circuit for 20
minutes. Afterwards the microslide is washed by Milli-Q water and soaked in 4% hydrofluoric acid solution (15 mL) overnight to remove the silica template. The resulting macroporous polymer is washed by Milli-Q water and air-dried. The macroporous polyaniline samples are flexible.

![Schematic diagram of the procedure for making macroporous PAN.](image)

Figure 3.4. A schematic outline of the procedure for making macroporous PAN.

Controlling the Size of Smaller Interconnecting Pores. For some polymers, by adjusting polymerization temperature it is possible to control the size of smaller interconnecting pores. A Fisher Isotemp 2150 circulator and an acrylic open bath are used to control the polymerization temperature of NOA-60. At low temperatures the prepolymer is very viscous and takes ~5 minutes to fill the template while at high temperatures they are less viscous, and fill the cell in several seconds. After the system equilibrates for thirty minutes in the isotemp bath, the monomer is polymerized by exposure to UV light as described above.
Characterization of the Macroporous Polymers. The macroporous polymers can be affixed to conductive carbon tape and prepared for scanning electron microscopy by sputtering a thin layer (3-4 nm) of gold onto the surface. A Philips XL30 ESEM has been used to evaluate the resulting macroporous polymers. The samples are broken using a sharp razor blade and are tilted 30-40° to obtain the cross-sectional images. In-situ Energy-Dispersive X-ray (EDX) analysis on the same ESEM is used to evaluate the amount of residual silica. To determine the diameter and standard deviation of smaller inner pores, over 200 pores are sized using SEM.

The optical properties of the macroporous poly(methyl methacrylate) films are evaluated by measuring their transmission spectra at normal incidence, using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer. Free-standing macroporous PMMA films are sandwiched by two microslides to ensure flatness. Pure PMMA films with the same thickness are used as references. For the refractive index matching experiments, macroporous poly(allyl methacrylate) films are used and the voids are filled with various fluids of known index prior to the optical measurements.

Results and Discussions

The quality of any material formed via template-directed synthesis depends sensitively on the order and properties of the starting template. Figure 3.1 shows a typical scanning electron micrograph (SEM) of the top and side views of one of our templates, a colloidal-silica single crystal. In this instance, 298 nm silica spheres are organized into a close-packed arrangement with long-range order both parallel and perpendicular to the glass substrate. While SEM provides a good picture of the sample
quality over 10 microns, the assessment of order over a larger range is best found in Fourier transform analysis of low magnification SEM (40×40 μm²). Such data is shown in the inset of Figure 3.1A; sharp peaks in the Fourier transform confirm long-range crystalline order. SEM studies over adjoining regions spanning more than 5 mm reveal no detectable grain boundaries.87 While it is clear that the samples are also crystalline in the cross-sectional view (Figure 3.1B), it should be noted that perspective views such as these cannot distinguish between the hexagonal close-packed structure (ABAB····) and the face-centered cubic structure (ABCABC····). This is because it is difficult to determine the exact angle of the cross-sectional view, which in turn makes it difficult to assess which crystal face is visualized in these images. Confocal microscopy of gravity sedimented colloidal crystals96 has indicated that the stacking between (111) planes is neither f.c.c. nor h.c.p., but a random arrangement. Theoretical calculations, though, have indicated that the f.c.c. structure is stabilized slightly even with completely non-interacting spheres.97,98 In future studies, where the transmission is investigated as a function of angle away from the normal, the exact nature of the crystal structure will be a more important issue.99,100

These silica-air crystals can serve as templates for the formation of macroporous polymers as illustrated in Figure 3.2. Figure 3.5 shows a typical SEM top and side view of a macroporous poly(styrene) film made by using a 330 nm silica colloidal crystal as a template. The material clearly has retained the three-dimensional crystalline order of the template and exhibits ordered close packing of air spheres in the polymer. Sharp peaks in the FFT of even larger length scale (40×40 μm², see the bottom inset in Figure 3.5A)
demonstrate the long-range crystalline order. The marks left by template silica balls shown in the upper inset of Figure 3.5A are clearly visible.

Membranes up to several square centimeters in area are easily prepared using larger template crystals. Figure 3.6 shows a photograph of a macroporous poly(methyl methacrylate) film grown using a 330 nm silica colloidal crystal as a template. The reflected colors are caused by Bragg diffraction of visible light by the array of air spheres. Several colors are apparent in the image. This is because the film is flexible and slightly curved in this example, so the angle of incidence of the illuminating white light varies with respect to the crystal planes.

Since the template crystals can be made with variable sphere sizes, as well as film thickness, the resulting macroporous polymers have easily controlled void volume and thickness. Figure 3.7 shows the SEM cross-sectional images of macroporous poly(methyl acrylate) films made by using 324 nm silica colloidal crystals of different thickness (10 layers for Figure 3.7A and 24 layers for Figure 3.7B) as templates. Films up to 50 microns can be made using these templates. An advantage of the thicker films is that they are sturdier and can be more readily handled as freestanding films. Figure 3.8 illustrates that these macroporous polymers can be made with different void sizes.
Figure 3.5. Scanning electron micrograph (SEM) images of a typical macroporous poly(styrene) membrane, formed using a 330.2 nm SiO$_2$ colloidal crystal as a template. (A) Top view (×8,000), with upper inset showing higher magnification (×100,000) and lower inset showing the FFT of a low magnification image of a 40 × 40 μm$^2$ region. (B) Side view (×6,000), with inset showing the interconnecting inner pores at higher magnification (×100,000).
Figure 3.6. A photograph showing the colors reflected from a macroporous poly(methyl methacrylate) (PMMA) film made by 330.2 nm silica template. The variation in color arises from the fact that the film is curved.
Figure 3.7. Typical scanning electron micrograph (SEM) cross-sectional images of two macroporous poly(methyl acrylate) membranes made using the same size (324.8 nm) silica templates with different thickness. (A) 10 layers (B) 24 layers.
An interesting feature of these samples are the smaller uniform inner pores, which interconnect the larger air spheres. Figure 3.8 shows SEM top views of macroporous poly(styrene) films made by using 260 nm and 330 nm silica single crystal as templates. These images are different from Figure 3.5A because the samples were prepared so that the interior layers of the polymer rather than the surface layers are visible. The smaller inner pores appear at nearly regular spacing in the polymer, wherever silica spheres were in closest proximity to one another. Over 200 inner pores were counted and sized in the SEM, providing average sizes and distributions. Figure 6a shows a sample with 55.8 ± 3.8 nm inner pores made by 260 nm template silica and Figure 3.8B shows a sample with 57.9 ± 4.3 nm inner pores made by 330 nm template silica. Some of these pores are missing or very small, likely the result of defects or silica spheres that were not in perfect contact. These defects, which are present at approximately 20% of the total sites, are not so prevalent as to disrupt the interconnected pore network.

The temperature of the initial monomer solution has a significant effect on the size of the internal pores. Figure 3.9 shows that the size of the smaller pores in macroporous NOA 60, a commercial polyurethane, could be varied through control of monomer temperature. For a given sample of silica colloidal crystals (353 nm diameter), very viscous NOA 60 at 22.5°C produced 117.6 ± 8.3 nm inner pores. Less viscous monomer at 40.0°C made 90.6 ± 6.5 nm pores and at 70°C, where the monomer was very fluid, inner pores of 60.7 ± 4.9 nm were produced. Other parameters, such as the shrinkage of the monomer upon polymerization, as well as its ability to wet the silica surface, had much less effect on the observed morphology.
Figure 3.8. Scanning electron micrograph (SEM) top view images of the inner layers of two macroporous poly(styrene) membranes made using silica templates with different sphere diameters. This shows the insensitivity of the size of the interconnecting inner pores to the size of the template silica spheres. (A) 260.4 nm silica template produced 55.8 nm (±6.8%) inner pores. (B) 330.2 nm silica template produced 57.9 nm (±7.4%) inner pores.
Figure 3.9. Scanning electron micrograph (SEM) top view images of the inner layers of three macroporous poly(urethane) membranes made using identical silica templates (353.0 nm sphere diameter) at different polymerization temperatures. This illustrates the systematic change in the sizes of the inner pores with polymerization temperature. This is attributed to changes in the viscosity of the prepolymer. (A) \( T = 70.0^\circ C \), pore diameter = 60.7 nm (±8.1%)  (B) \( T = 40.0^\circ C \), pore diameter = 90.6 nm (±7.2%)  (C) \( T = 22.5^\circ C \), pore diameter = 117.6 nm (±7.1%)
Not only macroporous nonconductive polymers can be made using templating strategy, but also conductive polymers. Figure 3.10 shows a SEM top view of a macroporous poly(p-phenylenvinylene) (PPV) sample made by using a 274-nm silica colloidal crystal as a template. The periodic voids, which lie at the original locations of the silica spheres, are clearly seen in the etched sample. Indeed, due to the shrinkage of the sample upon etching, the lattice is slightly distorted and the similar result has been reported previously. These larger voids are interconnected by smaller inner pores, whose sizes are much bigger than those of nonconductive polymers made from fluidic monomers as in Figure 3.8. The large diameters of these inner pores result from the high viscosity of the PPV precursor solution.

Figure 3.10. Scanning electron micrograph (SEM) top view image of the inner layer of a macroporous PPV membrane, made using a 274-nm silica colloidal crystal as a template.
Conductive macroporous poly(aniline) has also been fabricated using electrochemical synthesis. Figure 3.11 shows a SEM top view of a macroporous poly(aniline) sample made by using a 314-nm silica colloidal crystal as a template. The material clearly has retained the three-dimensional crystalline order of the template and exhibits ordered close packing of air spheres in the polymer.

![SEM image of macroporous poly(aniline) sample](image)

**Figure 3.11.** Scanning electron micrograph (SEM) top view image of the inner layer of a macroporous poly(aniline) membrane, made using a 314-nm silica colloidal crystal as a template.

Optical studies of these samples illustrate the diffractive properties of the matrix and provide additional evidence of the high crystalline quality of these samples. Optical transmission measurements are obtained at normal incidence to the films, parallel to the (111) crystallographic axis, using a commercial UV-visible spectrometer. Figure 3.12 shows the optical transmission spectra for three macroporous polymer samples made
from silica spheres ranging from 311 to 360 nm in diameter. A small incoherent scattering background was subtracted from this data in order to facilitate comparison with a theoretical model of photonic band gap behavior (dashed lines), described further below. Although the origin of this background is unclear, it does not appear to be related to point defects or surface roughness. In any event, it varies only slightly in the vicinity of the optical stop band, and thus does not substantially influence the measurements. Figure 3.13 shows the predicted peak position, $\lambda_{\text{max}}$, versus sphere diameter; again the data is in agreement with a model which assumes a perfect three dimensional lattice of ordered air spheres in a polymer matrix.

Similar to the thickness dependence of the optical properties of the ordered silica-air colloidal crystals as described in Chapter 1, the width of the stop bands of these macroporous polymers also display a dramatic dependence on film thickness. The observed narrowing of the stop band with increasing film thickness is reminiscent of the Debye-Scherrer effect in small crystallites. Here, the angular width of a diffraction line is limited by the highest spatial frequency accessible in the reciprocal lattice. The width is thus inversely proportional to the number of lattice planes, and arbitrarily narrow lines should be obtained by increasing the crystal thickness. However, in the air-polymer colloidal crystals studied here, the narrowing of the stop band saturates above a certain critical thickness. Further increases in film thickness do not result in narrower band widths. This result is summarized in Figure 3.14. Both types of sample reach their limiting bandwidths at thicknesses of ~10 layers.

One important issue for many applications is the net void volume, or surface area, in these systems; Energy-Dispersive X-ray analysis (EDX) of the macroporous films
show only trace amounts of silica (less than 0.7%) indicating that the treatment does remove almost all of the silica. This is not surprising due to high dissolution rate of silica in aqueous HF ($k_1 = 5 \times 10^{-8} \text{ g SiO}_2 \text{ sec}^{-1} \text{cm}^2 \text{M}_{\text{HF}}^{-1}$) and the internal connections between silica spheres. Additionally, the predicted optical spectra are highly sensitive to the volume fraction of the polymer. The predictions shown in Figures 3.12 and 3.13 assume that the air spheres are close-packed, and that the polymer fills the remaining $\sim 26\%$ of the total volume. The good agreement with experimental results provides further evidence that the polymer effectively templates against the colloidal crystal.

**Figure 3.12.** Experimental (solid lines) and calculated (dotted) optical transmission spectra at normal incidence of macroporous poly(methyl methacrylate) membranes. The diameters of the air spheres in the three samples are shown. All three calculated curves have been scaled by an overall multiplicative factor of 0.75, as described in the text. Otherwise, these calculations contain no adjustable parameters. The excellent agreement between the observed and calculated bandwidths is further evidence for the high quality of the samples.
Figure 3.13. Wavelength at which the optical transmission spectrum peaks, $\lambda_{peak}$, as a function of sphere diameter. The open circles are experimental points measured at normal incidence. The solid curve shows the calculated value of $\lambda_{peak}$ for the inverted macroporous structures, while the dashed curve shows the value for the silica sphere templates.
Figure 3.14. Experimental and calculated stop band widths as a function of the number of repeating layers of air/polymer macroporous films, with air sphere diameter of 284 nm. The polymer in this case is poly(allyl methacrylate) (PAMA), with a refractive index of $n = 1.64$, so these samples have $\psi_0 = -0.465$. The solid lines are calculated using the SWA, with no adjustable parameters.
Macroporous Polymers with Uniform Thickness and Pore Size.

A template method such as this one provides a simple and versatile route for the production of macroporous polymers. A comparison of Figures 3.1 and 3.5 clearly shows that the high quality of the initial silica colloidal crystals leads to high quality porous polymers. Moreover, since the template thickness and sphere size can be controlled, so can the macroporous structure. Void sizes ranging from 200 to 400 nm in diameter have been achieved, with good thickness uniformity across one centimeter in all cases (Figure 3.6). Monodisperse silica spheres can be made ranging from 30 nm\(^4\) up to several microns in diameter.\(^6\) If high quality templates of the larger and smaller silica can be prepared, then void sizes over the entire nanometer size range should be feasible.

An important issue for many applications of macroporous polymers, especially those prepared in a thin film format, is that the resulting films must be strong and resistant to cracking. While the mechanical properties have not been quantified here, this method allows for the use of any monomer whose resulting polymer is not soluble in hydrofluoric acid. Thus, glassy polymers (polystyrene, \(T_g \approx 94.8^\circ C\))\(^4\) as well as rubbery polymers (poly(urethane), \(T_g \approx 24.5-25.0^\circ C\))\(^5\) work equally well in templating against the colloidal crystal. In addition, the initial template can be prepared in thickness up to 50 microns. Macroporous methacrylate polymers made with these thickness are free standing and flexible. Template crystals can be prepared with even greater thickness (up to 1 mm); however their long-range crystalline order begins to degrade above 200 microns. In addition, polycrystalline colloidal crystals of silica are routinely prepared in millimeter capillary tubes as opposed to our planar thin film geometry.\(^6\) While such
samples would not be ideal for optical studies, they may be more suitable for other applications requiring macroporous media.

**Small Interconnected Pore Structure Arises from Monomer Wetting.**

Given the potential importance of the interconnection pores in non-optical applications, primarily separation technologies, we investigated whether and over what range their size could be controlled. From their placement in the larger voids it is apparent that these small pores are located where the template silica spheres were in closest proximity. One possible explanation for their origin is that the initial monomer solution could not wet the silica sphere surfaces completely, leading to gaps in its filling of the template. Fluid viscosity is known to be an important factor governing the effective filling of porous materials; more viscous liquids are less able to completely absorb into the available free space due to both wetting and capillary phenomena.\textsuperscript{107-110}

Alternatively, polymerization shrinkage could result in the formation of the pores. The three monomers employed in this work undergo 20-30 percent volume shrinkage upon polymerization;\textsuperscript{111} as the silica template is effectively incompressible, thin areas of polymer such as those located between spheres could yield due to shrinkage forming the pore structure observed.

To evaluate these issues, NOA-60, a particularly viscous monomer, was polymerized at different temperatures. Temperature has a large effect on monomer viscosity,\textsuperscript{84,112} and thus the monomer fills the porous template faster at higher temperatures. Figure 3.9 shows the systematic decrease in pore size as the temperature is increased. This observation illustrates that monomer viscosity is an important consideration in the formation of the smaller pores, and by manipulating this parameter
inner pore sizes can be controlled. Efforts to create smaller pores using very low viscosity monomers, however, were not successful and average pore diameters of 50 nanometers were typical. It may be that this lower limit is indeed the result of polymerization shrinkage. If so, the creation of inner pores whose diameters are smaller than 50 nanometers will require low shrinkage monomers.

Conductive Macroporous Polymers.

Because of the open structures and the high surface areas associated with macroporous conductive polymers, such materials may find important applications in electrochemistry, such as electrodes with high surface areas and electrochemical sensors.\textsuperscript{113-116} Macroporous PPV membranes with ordered submicron-sized void structures are potentially valuable for highly efficient light-emitting diodes (LED) and photodiodes technologies, as well as for polymer laser application.\textsuperscript{117-121}

Optical Properties of Macroporous Polymers.

Because of the ordering of the air spheres within the polymer, these samples exhibit diffraction phenomena that lead to striking optical properties. The most prominent is the presence of a strong diffraction peak in the optical spectrum. Certain basic properties of these systems can be well described by Bragg's law. At normal incidence (where \( \sin \theta_{inc} = 1 \)), the spectral position of the peak in the optical density, \( \lambda_{peak} \), can be found from:

\[
\lambda_{peak} = 2 n_{eff} d_{111},
\]

where \( n_{eff} \) is the average refractive index of the entire medium (air and polymer) at optical frequencies and \( d_{111} \) is the interlayer spacing of the air spheres along the (111) direction.
This spacing is related to the sphere diameter $D$ by $d_{111} = \sqrt{2/3} \ D$ for any close-packed structure.

While Bragg’s law explains the spectral position of the peak, a theoretical treatment appropriate to strongly diffracting layers is necessary to provide a quantitative model of the optical spectra. The scalar wave theory developed for periodic dielectric structures\textsuperscript{82,124} can be easily applied to these materials. In short, Maxwell’s equations are solved for a periodic dielectric assuming that one may neglect diffraction from all but one set of crystalline planes (in this case, the \((111)\) planes). While this approximation is not entirely correct, the model is tractable and is appropriate for comparison with normal-incidence transmission spectra. In particular, although this theory always predicts a larger optical density than observed, the predicted spectral bandwidths are in good agreement with observations.\textsuperscript{125} Thus, this formalism can be used to evaluate whether the observed bandwidths are controlled by defects in the sample or are intrinsic to the film. In principle, the calculation contains no adjustable parameters, since the size of the spheres and the sample thickness are independently determined from SEM measurements, and the refractive index of the polymer is known. However, because of the known difficulties in predicting the magnitude of the peak optical density, an overall multiplicative scaling factor is used. This facilitates comparisons of the measured and calculated bandwidths.

The predictions of the scalar wave approximation are compared to experimental data in Figure 3.12. The samples used to obtain these data (solid lines) were all thin, on the order of 9-12 layers. All three theoretical curves (dotted lines) have been scaled by a multiplicative factor of 0.75, but otherwise there are no adjustable parameters.
Remarkable agreement between theory and experiment provides evidence that these samples are not highly defective; in addition, it rules out the possibility that residual silica was left behind. Finally, optical characterization of this type illustrates that the film did not undergo significant dimensional changes during the HF treatment and thus faithfully reproduced the starting template. Figure 3.13 shows the predicted and measured spectral positions of the optical stop bands, as a function of sphere diameter, obtained from data such as that shown in Figure 3.12. The solid line is the prediction from the scalar wave theory, which is nearly identical to that obtained from Bragg's Law, equation [1] above, for films thicker than ~20 layers. For reference, the dashed line shows the predicted spectral positions for the templates ("normal" samples, with silica spheres surrounded by air, as opposed to "inverted" or macroporous samples). The ~100 nm shift between the two is a result of the substantial decrease in \( n_{\text{eff}} \), resulting from the lower volume fraction occupied by the polymer in the "inverted" samples.

Figure 3.14 shows that these air-polymer samples reach their limiting bandwidths at thickness of ~10 layers. We note that these limiting values correspond to fractional bandwidths of ~5%. This is typical of the widths observed in colloidal crystals, but is much broader than the widths encountered in other types of diffraction phenomena. For example, single crystal x-ray linewidths and reflection bandwidths of Bragg gratings in optical fibers can both be as narrow as 0.01% of their spectral position. One possible explanation for the broad widths observed here is that defects dominate the optical response, and prevent the observation of narrower natural linewidths. This seems unlikely, given the high sample quality. Alternatively, the bandwidth may be an intrinsic property of these strongly diffracting systems.
To evaluate this issue, the scalar wave model is used to calculate transmission spectra. The solid curve in Figure 3.14 represents the result of these calculations. Parameters used here include the air sphere diameter and number of sample layers, both determined from SEM measurements. The agreement between theory and experiment is remarkable, given that the SWA assumes an ideal, defect-free lattice. These results suggest that the broad bandwidths observed in these samples are a fundamental property of close-packed spherical arrays. This may be understood as follows. For crystals of high dielectric contrast, diffraction is very strong, and the amplitude of the radiation attenuates rapidly with propagation distance into the crystal. As a result, most of the incident radiation interacts only with a few lattice planes, near the surface. The measured bandwidth is determined largely by these interactions near the input facet, and not by the subsequent propagation through the medium. Thus, increasing the thickness of the crystal above a certain critical thickness has little effect on the bandwidth.

Zacharaisen has given an expression for the critical thickness, derived within the framework of dynamical diffraction theory; however, this result is derived under the assumption of small dielectric contrast, and is therefore not valid for these air-polymer systems. A more general result, valid for any \( \varphi_0 \), can be found from the SWA, as follows. The critical thickness \( N_c \), expressed as the number of (111) layers, may be defined by \( |k_{\text{max}}^i| N_c d_{111} = 1 \), where \( k_{\text{max}}^i \) is the imaginary part of the photon wave vector at the center of the stop band and where \( d_{111} \) is the \( \{111\} \) lattice spacing. For close-packed spheres, \( N_c \) is given by:
\[ N_c = \frac{1}{\pi} \cdot \left( \sqrt{4 + \left( \frac{K\psi_0}{1 + \psi_0} \right)^2} - 2 \right)^{-\frac{1}{2}} \]  

where \( K = \left( \frac{3}{p^2} \right) [\sin \beta - \beta \cos \beta] \), and where \( \beta = 2\pi \sqrt{\frac{3}{8}} \). For an air/polymer film made with PAMA (\( n = 1.64 \)), \( N_c = 6 \) layers. A consequence of this analysis is that, for a crystal of a given thickness, the bandwidth should be a sensitive function of the dielectric contrast. As mentioned previously, one can control the contrast by filling the interstitial pores of a air-polymer film with dielectric fluids. In this way, a range of different values of \( \psi_0 \) can be obtained for a single sample.\(^{127}\)

**Conclusions**

The fabrication of polymeric materials with ordered sub-micron-sized void structures is potentially valuable for many separation technologies as well as for emerging optical applications. This chapter describes the preparation of macroporous polymer membranes with regular voids and the characterization of their diffractive optical properties. These materials are made using a colloidal crystal template of silica microspheres; the air between the spheres can be replaced by monomers that can be subsequently polymerized. The use of silica microspheres as templates makes it possible to employ chemical rather than thermal methods for template removal. For this reason, polymers as diverse as polyurethane and polystyrene can be used to create freestanding macroporous films, with thickness ranging from 0.5 to 50 \( \mu \)m. Scanning electron microscopy of these samples indicates a well-formed porous structure consisting of voids ranging in diameter from 200 to 400 nm. These large cavities are not isolated, but rather interconnected by a network of monodisperse smaller pores (\( d = 50 - 130 \) nm) whose size
can be controlled by varying the polymerization temperature. These membranes exhibit striking optical properties due to the periodic arrangement of air spheres in the polymer medium. Normal-incidence transmission measurements of these samples are compared to a theoretical model based on a scalar wave approximation. This model assumes a structure of close-packed, three-dimensional air spheres ordered over long length scales. The good agreement between theory and experiment provides additional evidence of the long-range structure of these samples. These films, larger 100 nanometer voids connected by smaller pores, are reminiscent of many inorganic zeolites though with a much larger length scale. This suggests that these films may be valuable for large-molecule separation processes, where the interconnecting pores provide optimal flow and improved efficiencies.
References


Chapter 4

Preparation of Macroporous Metals with Ordered Arrays of Voids from Colloidal Crystal Templates

Introduction

Control over the three-dimensional microstructure of bulk solids offers great potential for the development of new materials with interesting and valuable properties. In particular, if such control is used to define a porous matrix within a solid, then the resulting materials can possess readily accessible internal surfaces. Template-directed syntheses have been broadly applied to the creation of both meso- and macroporous ceramics,\textsuperscript{1-8} carbons\textsuperscript{9} and polymers,\textsuperscript{10-14} which are valuable both because of their high internal surface areas as well as for their diffractive optical properties.\textsuperscript{4,13,14} Porous metals, made by similar methods, would be of particular value. High surface area metals in a variety of formats could be used in numerous applications, ranging from electrochemical sensors\textsuperscript{15-18} to catalytic converters.\textsuperscript{16} Moreover, recent work on lithographically prepared metallo-dielectric structures suggests metals with well-ordered porous networks have recently been demonstrated to have photonic band gaps at microwave and infrared wavelengths, and can be used as optical filters.\textsuperscript{19-30} Thus it is of great interest to develop chemical methods for creating macroporous free-standing metals, especially with highly ordered porous structures.

The application of templating methods to the synthesis of macroporous metals is in its early stages, though the general area of template chemistry has been quite active
over the last decade. The term templating refers to a technique which involves first the
formation of a temporary medium, the template, whose interstices are subsequently filled
with another material. The template is then removed chemically or thermally, leaving
behind a porous material that is an inverse replica of the template's microstructure. The
architecture and form of the resulting porous sample thus depends directly on the
characteristics of the starting template. Templates for the production of mesoporous
materials, i.e. materials containing pores with diameters less than 50 nm, include liquid
crystalline surfactant assemblies\textsuperscript{18,31-34} and anodically etched alumina
membranes.\textsuperscript{15,16,35,36} Such materials can be used to form high surface area metals with
pore sizes of 10-50 nm, typically with cylindrical voids.\textsuperscript{15,16,18,37-41}

Colloidal crystalline films are ideal starting templates to make porous metal films
with highly ordered void structures in a free-standing format. But uniform deposition of a
metal into the interstitial regions of a colloidal crystal multilayer is a challenging
chemical problem. Existing examples of metal deposition into lyotropic liquid crystal\textsuperscript{18}
and anodic alumina\textsuperscript{16,36} templates, exploit flat and conductive surfaces to catalyze metal
formation. Such surfaces are not available in the interstitial regions of colloidal crystals
which are narrow and relatively inaccessible. Also, these templates as made are relatively
fragile and easily disrupted by agitation or gas evolution during deposition.

To overcome these obstacles, several methods have been developed to make
macroporous metals from colloidal crystals. The general scheme of Stein and
coworkers\textsuperscript{42-44} exploits differences in the solubility of metal salts to precipitate nickel
ions inside a template; these ions can then be reduced into metals or converted into metal
oxides. First, a polystyrene (PS) colloidal template is impregnated via capillary action
with a solution of metal acetate in either acetic acid or a water/ethanol mix. The solvent is removed by vacuum filtration leaving behind a PS/metal acetate composite. This composite is soaked in oxalic acid, resulting in the formation of an insoluble metal oxalate that is then heated in air or nitrogen. Application of heat (calcination) achieves two outcomes: removal of the PS template and conversion of the metal salt into either an oxide (air) or native metal (nitrogen). The macroporous metal oxides can also be partly or completely converted to macroporous metals by further calcination in hydrogen. Partial calcination results in a metal/metal oxide composite where control over the ratio of metal to metal oxide is achieved by varying the calcination conditions. While CO and CO₂ gases are evolved during heating, no apparent disruption of the lattice occurs, perhaps because the high temperature simultaneously promotes grain growth in the underlying porous lattice. The resulting porous metal contains monodisperse voids ranging in diameter from 250-500 nm. Similar oxalate chemistry should also be successful at making other macroporous metals.

Velev and coworkers⁴⁵-⁴⁷ and Mallouk and coworkers⁴⁸ use a filtration technique both to create the PS or silica colloidal crystal (with PS diameters from 30-1000 nm) and then to draw a solution of platinum or gold nanocrystals into the interstices of the crystal. The small size of the nanocrystals allows them to penetrate into the colloidal multilayer. At this point the composite metal/colloid crystal can be detached from the filter and dried in air. Removal of the PS and silica beads is accomplished either by calcination, yielding macroporous gold, or by hydrofluoric acid etch, yielding meso/macroporous samples. Pore size can be controlled by varying the size of the
nanoparticles (smaller particles yield thicker walls and smaller pores). This method may be adaptable to other nanocrystalline metals.

Wiley and coworkers\textsuperscript{49} and Vos and coworkers\textsuperscript{50} use electrodeposition technique to create macroporous nickel and gold within close-packed silica and PS sphere arrays. Before electrodeposition, a thin copper film has to be deposited on one side of the colloidal crystal\textsuperscript{49} or the colloidal crystal is directly deposited on a conductive ITO glass slide. In this chapter, we describe a method using gold nanocrystals to catalyze the electroless plating of metals (copper, nickel, gold, platinum, or silver) within the close-packed array of colloidal silica spheres which serves as a template for the growth of macroporous metals, specifically materials with pore diameters between 200 to 1000 nm, with highly ordered void structures in a free-standing format; the resulting macroporous films are free-standing, thermally stable and exhibit diffractive optical properties at visible wavelengths.

**Experimental Sections**

**Materials and Substrates.** All solvents and chemicals are of reagent quality and are used without further purification except for tetraethoxysilane (Alfa, 99%) which is freshly vacuum distilled before use. 200 proof ethanol is obtained from Pharmaco Products. 29.6% ammonium hydroxide and 49% hydrofluoric acid are obtained from Fisher. Ultra-pure water (18.2 MΩcm\textsuperscript{-1}) is obtained from a Millipore Ultra-pure Water System. Hydrogen tetrachloroaurate (III) trihydrate (99.9+%) is purchased from Aldrich. Tetraoctylammonium bromide, sodium borohydride and dodecanethiol are all obtained from Aldrich. 3-mercaptopropyltrimethoxysilane (3-MPTMS) is purchased from Gelest.
Electroless copper and platinum plating baths are prepared using standard recipes;\textsuperscript{51} electroless gold (Oromerse SO, Technic Inc., RI), nickel (EN 9148 low phosphorus, Technic Inc., RI) and silver (HE-300, Peacock Laboratories, Philadelphia, PA) plating baths are commercially available. 20 ml scintillation vials and glass microslides (75\times25\times1 mm) are obtained from Fisher and cleaned in a chromic-sulfuric acid cleaning solution (Fisher) overnight, rinsed with Milli-Q water (18.2 MΩcm\textsuperscript{-1}), and dried in a stream of nitrogen.

**Instrumentation.** Scanning electron microscopy and EDAX are carried out on a Philips XL30 ESEM. A CrC-100 sputtering system has been used to sputter a thin layer (3-4 nm) of gold on the samples before SEM analysis. Transmission electron microscopy is carried out on a JEOL 2010 operating at 200kV. XRD is performed on a Siemens D5000 diffractometer using Cu K\textsubscript{α} radiation and a Rigaku Geigerflex using Mo K\textsubscript{α} for the copper film. BET experiments are performed on a Coulter SA3100 using nitrogen absorption. Lindberg TF55035A tube furnace with quartz tubes and a vacuum system is used for heating studies.

**Colloidal Silica Synthesis and Surface Modification.** Monodisperse SiO\textsubscript{2} nanospheres are synthesized following the Stober-Fink-Bohn method.\textsuperscript{52} Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviation smaller than 5% are obtained through strict control of the reaction conditions.\textsuperscript{53} The surface of the freshly prepared colloidal silica is modified by coating a coupling agent, 3-mercaptopropyltrimethoxysilane (3-MPTMS) using the technique described by Philipse et al.\textsuperscript{54} A mixture of 200 ml freshly prepared silica alcosol and 10 ml 3-MPTMS is stirred at room temperature for 30 min. Then \(\sim\)160 ml solvent is slowly distilled off for
30 min. Then 100 ml 200 proof ethanol is added and the mixture is distilled again. The surface modified silica alcoslols are then diluted to 200 ml and washed with 200 proof ethanol by repeated centrifugation (at 4200 rpm) and ultrasonic dispersion cycles in order to remove impurities, such as ammonia, water, unreacted TEOS and 3-MPTMS. Six cycles are usually performed. The final centrifugation cakes are redispersed in 200 proof ethanol and the purified 3-MPTMS-silica alcoslols can be stored in sealed bottles for over years.

**Preparation of Thio-Derivatised Gold Nanoparticles.** An aqueous solution of hydrogen tetrachloroaurate (0.3544 g, 30 ml, 30 mmol dm$^{-3}$) is mixed with a solution of tetraoctylammonium bromide in toluene (2.1872 g, 80 ml, 50 mmol dm$^{-3}$). The two-phase mixture is vigorously stirred until all the tetrachloroaurate is transferred into the organic layer and dodecanethiol (0.2012 ml, 170 mg) is then added to the organic phase. A freshly prepared aqueous solution of sodium borohydride (0.3783 g, 25 ml, 0.4 mol dm$^{-3}$) is slowly added with vigorous stirring. After further stirring for 3 hours the organic phase is separated, evaporated to 10 ml in a rotary evaporator and mixed with 400 ml ethanol to remove excess thiol. The mixture is kept for 4 hours at -18°C and the dark brown precipitate is filtered off and washed with ethanol. The crude product was dissolved in 10 ml toluene and again precipitated with 400 ml ethanol. Finally the gold nanoparticles (~0.2 g) is dissolved in 10 ml toluene and the solution is stable for over years.

**Preparation of the Electroless Plating Baths.** Copper electroless plating bath is prepared as before by dissolving 0.938 g CuSO$_4$·5H$_2$O, 0.8 g NaOH and 3.759 g potassium sodium tartrate tetrahydrate in 20 ml Milli-Q water. Silver electroless plating bath is prepared as two parts: 0.2 g AgNO$_3$ and 1 ml 29% ammonia are dissolved in 10
ml Milli-Q water for part A; 0.4 ml 37.5% formaldehyde is diluted to 2 ml with Milli-Q water for part B. Nickel electroless plating bath is prepared by dissolving 0.537 g NiSO₄·6H₂O, 0.5 g NaH₂PO₄, 0.5 g HOCH₂COOH in 20 ml Milli-Q water. The pH of the solution is controlled to 6-7 by adding small amount of CH₃OONA and NaOH. Platinum electroless plating bath is prepared as before.¹⁶ 2.102g H₆PtCl₆·xH₂O and 0.5g NaOH are dissolved in 100ml Milli-Q water and the solution is then boiled to about 50ml and then diluted to 100ml again. 0.025 g NaOH and 0.05 g ethylamine are then dissolved in 5 ml above solution. Gold electroless plating bath (Oromerse SO, Technic Inc., RI) is commercially available.

**Fabrication of Macroporous Metals from Colloidal Crystals.** 3-mercaptopropyltrimethoxysilane (3-MPTMS) modified silica particles are assembled into three-dimensionally ordered planar colloidal crystals with thickness ranging from several layers to 10 μm by the methods described in Chapter 1 and our previous paper.¹⁷ The colloidal crystal film is then dipped into gold nanocrystals (∼ 0.02 g/ml in toluene) and air-dried for four times. Unattached gold is washed away by a rinse with toluene leaving a purple-grey film. The sample is then sintered by a propane torch (Turner, ∼ 900°C) for 4-6 minutes or in an oven at 575°C under air for eight hours resulting in a red gold-silica composite. Finally, the template is immersed in an electroless plating bath: for copper, 2ml 37.5% formaldehyde aqueous solution is added to the copper electroless plating bath to initiate the electroless deposition; for silver, part B is added drop by drop to part A; for nickel, the electroless plating bath is heated to 87°C in a water bath to initial the reaction; for platinum, a drop of hydrazine hydrate is added to the electroless bath; for gold, the electroless plating bath is heated to 70°C to start the electroless deposition. After several
minutes, during which time gas bubbles are visibly apparent, the template appears metallic and shiny. The silica is etched out by 2% (v/v) HF solution. The self-supported, iridescent macroporous metal film can be peeled off the glass slide within minutes and then are washed with Milli-Q water and air dried.

**Characterization of the Macroporous Metal Films.** The macroporous metal films can be affixed to conductive carbon tape for scanning electron microscopy. A Philips XL30 ESEM has been used to evaluate the resulting materials. The samples are broken using a sharp razor blade and are tilted 30-40° to obtain the cross-sectional images. *In-situ* Energy-Dispersive X-ray (EDX) analysis on the same ESEM is used to evaluate the chemical compositions. For transmission electron microscopy, the films are broken in toluene using an ultrasonic bath (Fisher, 40 W) for 1 minute and then a drop of the solution is deposited on Formvar-coated electron microscope grids. The latter are examined using a JEOL 2010 operating at 200kV. BET experiments were performed on a Coulter SA3100 using nitrogen absorption. Thicker samples were prepared for BET using a filtration method to make the silica colloidal crystal, which was then exposed to gold nanoparticles and annealed at 800°C for 2 hours before templating by methods described above. A Digital Instruments IIIA force microscope operating in Tapping Mode™ is used to image the surface features of the macroporous metal films. Due to the large changes in surface height, AFM imaging of these samples requires the use of very light tapping conditions, with setpoints held at nearly 100% of the free-amplitude vibration of the cantilever.

The diffraction of macroporous platinum films under white-light illumination are collected in a backscattering geometry; light was incident on the sample at 44°, and
diffracted light was collected at 65°. An f/2 optical system is used to collect the light, which is then imaged into an ISA HR 460 monochromator equipped with a CCD camera. Raw intensities (I) are corrected for instrument response by dividing by the reflection from a non-porous flat film of the same metal (I₀).

Results and Discussions

Fabrication and Characterization of Macroporous Metals using Colloidal Crystals as Templates. The characteristics of the starting template are central in defining the architecture and form of a macroporous sample. As we are concerned with creating crystalline porous networks within free-standing metals, it is necessary that the templates be highly ordered and of uniform thickness. Colloidal crystal multilayers are ideal substrates that meet these requirements. Unlike lyotropic liquid crystalline templates which typically provide mesoporous (d = 1-50 nm) arrays of cylindrical channels,¹⁸,³¹ colloidal templates produce meso- and macroporous (d = 30-1000 nm) samples containing interconnected spherical voids.¹-⁵,⁹,¹¹-¹⁴,⁴⁸,⁵⁸ Samples made from colloidal templates can be free-standing, and often exhibit visible diffraction due to their long range order.⁴,⁹,¹³ Although colloidal templates prepared using standard methods such as gravity sedimentation and filtration do contain single crystalline domains, they are comprised of a mosaic of these grains within pellets of non-uniform thickness.⁴,⁹,⁵⁹,⁶⁰ We use a convective self-assembly process⁵⁷ (see Chapter 1) which exploits capillary forces within a meniscus to drive crystallization to ensure that our templates are single crystalline and uniform as shown in Figure 4.1.
Figure 4.1. Typical SEM image of a silica colloidal crystal template made by convective self-assembly.

As can be seen in Figure 4.1, the thick template arrays consist of close-packed silica spheres; the resulting interstitial areas are curved, narrow and not readily accessible. Uniform deposition of a metal into these regions is a challenging chemical problem; most solution-phase chemistries which form metals do so on flat and conductive surfaces.\textsuperscript{49,50} In insulating templates with more accessible pores, metal formation can be catalyzed by the underlying surface.\textsuperscript{18,61} However, for the constricted and tortuous pores of our colloidal templates, such methods are unsuitable, and reactions which can deposit solid metal even in the absence of a continuous and conductive surface are more viable. One such method is electroless deposition. This solution-phase process is used commercially for plating metals onto flat insulating surfaces,\textsuperscript{51,55,62} and has been used to coat platinum on the sidewalls of narrow channels within alumina membranes.\textsuperscript{61} The
adaptation of electroless deposition to metal plating of colloidal templates poses two specific challenges. First, the technique requires the presence of catalytic sites which must be uniformly distributed within the porous array to ensure a complete filling of metal. Second, during electroless deposition reactions there is a vigorous evolution of byproduct gas which can disrupt the relatively fragile colloidal templates.

To address these two issues, we use metal nanocrystals rather than large flat surfaces as catalysts\textsuperscript{51,55,62} and strengthen our template by subjecting it to a high temperature treatment prior to filling. The process is outlined in Figure 4.2. First, colloidal silica is coated with a coupling agent, 3-MPTMS,\textsuperscript{53,54,63} which leaves a free thiol functionality at the surface. After convective self-assembly of the thiol coated silica colloids into arrays onto glass substrates, the templates are immersed in a toluene solution containing gold nanocrystals\textsuperscript{64} that affix to the colloidal surfaces at the thiol sites.\textsuperscript{65} These nanocrystals have average diameters of only 5 nanometers and are small enough to penetrate the tiny pores of the template matrix uniformly. Then, the silica-nanocrystal composite is heated in air using a propane torch (~900°C) for 4-6 minutes or in an oven at 700°C under air for three hours. The sintering plays two roles here: one is to strengthen the film to prevent it from fracturing during the gas evolution from electroless plating. The other is to burn off the organic coating of gold nanoparticles and expose the bare Au surface. Although the glass slide may soften during the sintering process, SEM results show this does not affect the long-range ordering of the colloidal crystal. Also, silica particles shrink in size by 6% to 10% during this heat treatment.
Figure 4.2. Scheme for the formation of macroporous metals by gold nanocrystal catalyzed electroless deposition.

Figure 4.3A shows a TEM image of a single colloid without 3-MPTMS modification isolated from the array after exposure to gold nanoparticles. It's obvious that the gold nanocrystals do not deposit on its surface. Figure 4.3B shows an isolated 3-MPTMS modified silica colloid after heat treatment. The gold nanoparticles are affixed to the colloid surface and are larger than those originally deposited. Once sintered, template arrays can be subjected to a variety of electroless deposition baths for the formation of solid copper, gold, platinum, silver or nickel. Figure 4.4 shows an example of an isolated section from an array after partial exposure to a copper electroless deposition bath. The thicker metal film, which is copper, curves around the contours of the sphere as expected for a template process. After metal is deposited in the interstitial
areas, the silica can be etched away by a mild hydrofluoric acid rinse leaving behind a macroporous metal.

**Figure 4.3.** Typical TEM images of isolated colloidal silica spheres after exposure to gold nanoparticles. (A) Bare silica without gold nanocrystals attached. (B) 3-MPTMS coated silica with gold nanocrystals attached after heat treatment. The nanocrystals effectively bind to the free thiols at the colloidal surfaces with a coverage of $\sim 20\%$.

**Figure 4.4.** TEM image of partially plated colloids after short exposure to a copper electroless deposition bath.
The uniformly distributed gold nanoparticles within the 3-MPTMS modified silica array are critical to ensure a complete filling of metal. Figure 4.5 shows an incompletely filled copper sample using bare silica colloidal arrays as template. Figure 4.6 shows SEM images of the complete macroporous metal films using 3-MPTMS modified silica as template. The cavities match the size of the starting silica colloids and retain their close-packed ordering. Higher magnification images of the structure show that each larger cavity in these materials is connected to its twelve neighbors by smaller pores of 60 nm ± 10 nm diameter (inset in Figures 4.6B). Based on their location and number, connecting pores appear to form around the points where the original silica spheres once touched; such a morphology has been observed for other porous materials made using colloidal crystal templates.1-5,9,11-14,48,58 The long range order of the voids is apparent from Fourier transforms (FFTs) of these images. Figure 4.6B shows two FFTs computed from micrographs of macroporous platinum taken over 8 millimeters apart. Not only do these FFTs show the spot pattern expected for a perfect hexagonal array, but their orientations are nearly coincident. Parallel dashed lines indicate one reference direction; their alignment with FFT spots in both cases demonstrates the absence of grain boundaries over mm distances. Images taken at intermediate points also show similar orientation, indicating that the hexagonal arrangement of the voids contains no grain boundaries over length scales as long as millimeters.57
Figure 4.5. Typical SEM image of an incompletely filled macroporous copper sample using bare silica array as template. Without gold nanocrystals, electroless deposition does not proceed completely.
Figure 4.6. Typical scanning electron micrographs (top view) of two macroporous films. (A) A macroporous silver film made from a colloidal template (353 ± 17 nm diameter). The Fourier transform (FFT) of an image (15.75 × 11.75 μm area) (inset) shows the long-range hexagonal order. (B) A macroporous platinum film (318 ± 13 nm diameter voids). The bottom left insets show FFTs of two images (15.75×11.75 μm area) taken at opposite corners of a 4x8 mm region. The upper right inset SEM image shows the interconnected pores and rough surface of the same sample.
An important issue for this chemistry is the extent to which the metals infiltrate the template; cross-sectional images of these materials and measurements of their average surface area provide ample evidence that these samples are uniformly porous. Figure 4.7 shows cross-sectional micrographs of two macroporous metal samples; in both cases, the spherical voids extend throughout the sample with no bubbles or gaps. Surface area measurements of bulk samples are also consistent with the observed morphologies (see Table 4.1). If metal deposition had not occurred fully throughout the templates, then the films would possess larger internal cavities which would lower the internal surface areas. The measured surface areas, which are calculated by assuming spherical air particles (215 nanometer diameter) fill 74% of the volume of the metal and no attempt is made to correct for the loss of surface area caused by the interconnections between pores, or for the enhancement of surface area due to surface roughness, however, are in good agreement or are even larger than those calculated from a model that assumes close-packed smooth air cavities (Table 4.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Calculated Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>26</td>
<td>11.8</td>
</tr>
<tr>
<td>Cu</td>
<td>12</td>
<td>9.8</td>
</tr>
<tr>
<td>Ag</td>
<td>12</td>
<td>10</td>
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</tbody>
</table>
Figure 4.7. Cross-sectional SEM images of two macroporous metal films. (A) A macroporous copper sample made from a colloidal template (325 ± 15 nm diameter) reveals the porous morphology throughout the films. The inset SEM image shows the interconnecting pores and smooth surface of the same sample. (B) SEM image of a nickel sample made from a colloidal template (353 ± 17 nm diameter) with 15 colloidal layers.
The crystallinity and chemical composition of the metals can be evaluated using energy dispersive x-ray analysis (EDX) and x-ray diffraction. EDX of the cross-sections of these films demonstrate that the electrodeposited metals are quite pure (Table 4.2). Only small amounts of silicon are detected indicating the complete removal of the template. Gold concentration is low despite its use as a catalyst. This is reasonable since if we assume a 20% coverage of the silica spheres with 5 nanometer gold particles, only about 10% of the internal volume should be comprised of gold. However, most of this gold will reside at the exposed surfaces of the metal, and lower the effective surface areas of the active metals by 20%. X-ray diffraction analysis shows diffraction peaks characteristic of polycrystalline metallic films as shown in Figure 4.8. Domain sizes in these samples range from 20-30 nanometers for silver, platinum and gold to 1-3 nanometers for copper and nickel (Table 4.3). This result explains why the measured surface areas are systematically larger than those calculated: the calculation assumes smooth spherical cavities, and does not account for the surface roughness present in these polycrystalline materials.

Table 4.2. Energy-Dispersive X-ray (EDX) analysis of the macroporous metal films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>Si</th>
<th>Au</th>
<th>metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.6 ± 0.9</td>
<td>0.7 ± 0.4</td>
<td>0.8 ± 0.5</td>
<td>93.7 ± 1.3</td>
</tr>
<tr>
<td>Cu</td>
<td>5.8 ± 1.1</td>
<td>1.2 ± 0.7</td>
<td>1.8 ± 0.8</td>
<td>91.3 ± 0.7</td>
</tr>
<tr>
<td>Ag</td>
<td>2.8 ± 1.2</td>
<td>2.3 ± 1.0</td>
<td>2.5 ± 0.6</td>
<td>92.5 ± 1.4</td>
</tr>
<tr>
<td>Au</td>
<td>1.7 ± 1.0</td>
<td>1.2 ± 0.3</td>
<td></td>
<td>95.1 ± 1.3</td>
</tr>
<tr>
<td>Pt</td>
<td>1.6 ± 0.4</td>
<td>0.6 ± 0.2</td>
<td>0.8 ± 0.3</td>
<td>94.9 ± 0.8</td>
</tr>
</tbody>
</table>
Figure 4.8. Powder x-ray diffraction patterns of macroporous metal films. Backgrounds for copper are not flat due to the fact that a single crystal diffractometer optimized for narrow angle data collection was used rather than a machine designed for powder diffraction.
Table 4.3. Nanocrystalline particle size by X-ray diffraction before and after heating treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before heating (nm)</th>
<th>After heating (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2 ± 0.5</td>
<td>47 ± 4</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>27 ± 2</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>32 ± 3</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>21 ± 2</td>
<td>32 ± 3</td>
</tr>
</tbody>
</table>

One consequence of these small grain sizes is that the as prepared samples are not very stable either mechanically or thermally; vigorous sonication (40 W, 5 minutes) fractures the films and, in the case of the nickel and copper, completely destroys their porosity. Moreover, thermal treatment of macroporous nickel results in a reduction of porosity at temperatures of only 500°C. The stability of the macroporous metal can be improved by thermal treatment of the metal-silica composite prior to silica removal. This treatment causes significant grain coarsening in all metals (see Table 4.3), yet has little effect on the long range order and morphology of the pores. Once sintered, macroporous nickel is able to withstand prolonged sonication as well as heating under vacuum to 500°C without any loss of porosity; macroporous platinum retains its porosity up to temperatures of 1000 °C in air as shown in Figure 4.9A, while the same sample loses their porosity if not has been sintered (Figure 4.9B).
Figure 4.9. Typical SEM images of a sample being heated at 1000°C in air for 16 hours. (A) Pre-sintered at 500°C for 8 hours. (B) Not pre-sintered.

Optical Characterization of Macroporous Metal Films. These macroporous films exhibit striking iridescence in white light. Figures 4.10A and 4.10B show photographs of a macroporous platinum sample taken from two different angles. The uniformity of the colors in these images illustrates that the films are flat and ordered over their entire surface. Atomic force microscopy of the surface topology shown in Figure 4.11 illustrates that the walls between voids are sharply peaked and that the surface is hexagonally ordered; this ordering gives rise to the diffraction of visible light seen in the photographs. The diameters of the spheres in the original template control the surface periodicity and thus the diffractive properties of the macroporous samples. Figure 4.12A and 4.12B show the spectrally resolved diffraction from two macroporous platinum films made from two different sphere sizes; as expected, the sample made with smaller spheres
shows diffraction at shorter wavelengths. If these high quality samples can be fabricated with smaller (10-40nm) void sizes,\textsuperscript{10,67} diffraction would occur at soft x-ray wavelengths. Such films may prove valuable in x-ray optical applications.

**Figure 4.10.** Photographs of the same Pt film (pore size = 353 nm) at two different angles. Photographs were taken at mid-day under direct sunlight using 50 ASA slide film for high quality color reproduction. In A the sample is rotated \(\sim 16^\circ\) from horizontal; film B is rotated \(\sim 30^\circ\).

**Figure 4.11.** Atomic force microscopy of the surface topology of macroporous platinum. Void diameters measured from this image (d = 410 nm \(\pm\) 62 nm) agrees with the void diameter as determined from SEM (d = 353 nm). The cross-section shown beneath the image shows the walls that separate the voids. The widths of the walls are convolved with the tip radius; for this work, TESP silicon cantilevers (DI, Santa Barbara) with nominal tip radii of 50 nm were used as probes. Deconvolution of this tip radius with the observed data provides an estimate of 40 nm for the wall thickness at its narrowest point.
Figure 4.12. Diffraction of two macroporous platinum samples with different pore sizes under white-light illumination.

Applications for Macroporous Metals. The visible appearance of these samples, illustrated in Figure 4.10, suggests their potential in optical applications. As mentioned earlier, their appearance arises from light diffraction from the microstructured metal. This diffraction occurs only within the top surface of the films, however, since at visible wavelengths metals are opaque and these samples possess a complex two-dimensional topography with sharply peaked metallic features arranged on a hexagonal pattern (Figure 4.11). A quantitative description of the reflectance spectrum from such a surface requires a theoretical model; however, qualitatively the materials behave as expected. For example, films created with smaller voids have a maximum reflection at shorter
wavelengths (Figure 4.12, lower panel). Also, in contrast to commercial broadband gratings, these samples reflect over a fairly narrow range of wavelengths. This may result from the very high aspect ratios of the surface features, as seen in Figure 4.11. One-dimensional gratings with steeply etched features, or blazed gratings, are known to allow for very efficient reflection over a narrower range of wavelengths than less steeply etched surfaces.\textsuperscript{68-70}

Since metals are opaque, it is natural to consider the reflective properties of these films; however, there is evidence that metal films appropriately structured on the nanometer and micrometer level can manifest unusual transmission behavior.\textsuperscript{16,71,72} Metallodielectric structures, for example, are periodic arrays of metallic and non-metallic materials.\textsuperscript{21,73} Here, because of the periodicity and symmetry of the metal, light can be transmitted through a thin film.\textsuperscript{74} However, transmission is prohibited at wavelengths for which Bragg diffraction conditions are met and thus the system can be engineered to exhibit broadband optical filtering in the infrared region. This feature is in great demand for applications ranging from thermophotovoltaic energy conversion to telecommunications.\textsuperscript{75,76} The structures of the macroporous metals discussed in this work are in many ways analogs to these lithographically prepared materials, though with a smaller feature size and higher dielectric contrast. They could potentially be used in similar applications, and could allow for the fabrication of large-area optical components.

Macroporous metals are also potentially valuable in numerous non-optical technologies due to their large and accessible surfaces. A 500-micron film of macroporous gold that is 1 cm in diameter, for example, contains a surface area of roughly 5 square meters. Like many porous electrodes already in use, these macroporous
metallic films would greatly increase the sensitivity of an electrochemical sensor to an analyte.\textsuperscript{18,77} However, unlike many existing high surface-area electrodes, their open and interconnected morphology would allow larger molecules to easily diffuse to the electrode surfaces. Catalytic applications may also benefit from the open porous structure of these materials, as well as the nanocrystalline structure of the metal walls.\textsuperscript{78-81} Finally, we note that while the metal films are sturdy enough to be handled and to withstand sonication after heating, prior to this treatment, however, a nanocrystalline dispersion can be produced by sonication. Thus macroporous metals may provide an avenue to forming metal nanocrystals, such as copper and nickel, that are difficult to produce using direct chemical methods.

**Conclusions**

This chapter demonstrates the fabrication of free-standing macroporous metal films using colloidal silica crystals as templates. Porous metals have been prepared containing interconnected and monodisperse spherical voids with diameters ranging from 200 to 350 nanometers. The method uses gold nanocrystals to catalyze the electroless plating of metals (copper, nickel, gold, platinum, or silver) within the template and demonstrates a general strategy for extending template chemistry to an important class of solids. These samples possess high internal surface areas which are accessible via an interconnected pore network; this morphology may be of value in applications which rely on the chemical activity of metal surfaces. The accessible internal surfaces of these samples may be valuable in applications that rely on the catalytic or electrical activity of
metal surfaces, and the long range ordering of the voids endows the samples with tunable diffractive properties of potential interest in optics.
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Chapter 5

A Modern Nanoscale Lost-Wax Approach to Prepare

Single-Crystal Colloidal Crystals and Monodisperse Colloids

Introduction

The fascination with the monodisperse colloids dates back to more than a century when Faraday studied gold sols, the brilliant colors of which depend on the particle sizes. Originally, uniform dispersed matter attracted the interest of scientists essentially for academic reasons; i.e. to quantitatively interpret physical properties or surface interactions as a function of the morphology, size and other characteristics of such systems. Presently, the importance of well-defined colloids has been recognized in numerous applications, including ceramics, catalysis, pigments, magnetic recording materials, medical diagnostics, electrophoretic inks among others, mainly due to their uniform physical and chemical properties. These dispersions are also ideal model systems for colloid and surface science. They allow for the quantitative evaluation of the optical, magnetic, electrokinetic, or adsorptive behavior of colloidal matter as well as for the theoretical interpretation of the interactions that involve such particles.

Many advances in this area were brought on by the elaboration of simple, convenient, and reproducible methods that were able to generate monodispersed colloidal samples in relatively large quantities. Perhaps one of the biggest advantages of monodisperse colloids is their ability to form colloidal crystals. When sedimented, these
highly monodispersed colloids can form three-dimensionally periodic colloidal crystals with interesting and useful functionalities not only from the constituent materials but also from the long-range, mesoscopic order that characterizes periodic structures.\textsuperscript{13,19-31} A natural opal, for instance, is beautifully iridescent in color because silica colloids have been organized into a three-dimensionally ordered array with a lattice constant that is comparable to the wavelength of visible light (400-800 nm).\textsuperscript{32} Colloidal crystals have been the focus of great interest recently because of their potential use as optical filters and switches \textsuperscript{33-36}, chemical and biochemical sensors \textsuperscript{37-39}, high-density magnetic data storage devices,\textsuperscript{10,11,40} removable templates to generate highly ordered, macroporous materials\textsuperscript{41-53} and photonic crystals \textsuperscript{19,41,54-57}. Significant progress has been made with regard to the formation of colloidal crystals. A rich variety of methods are available for organizing monodispersed colloidal spheres into highly ordered three-dimensional arrays, such as gravity sedimentation,\textsuperscript{24,29,58-60} electrostatic interactions,\textsuperscript{20,29,31,36,61-64} physical confinement,\textsuperscript{19,65,66} colloidal epitaxy,\textsuperscript{26,67} electrophoretic assembly,\textsuperscript{21,23,27} and convective self-assembly.\textsuperscript{68-74}

These methods for preparing colloidal crystals have to manipulate the chemistry of colloid formation and colloidal crystallization conditions. Only silica and some polymer colloids, however, can be routinely prepared with the narrow size distributions required for forming high quality colloidal crystals.\textsuperscript{19,29} Unfortunately these colloids do not exhibit valuable optical, nonlinear optical, or electro-optical functionality. In addition, colloidal crystallization is a difficult issue for other denser colloids even when they are routinely available.
To extend significantly the availability of monodisperse colloids and their colloidal crystal, we developed a physical rather than chemical templating strategy. In fact, the strategy for using easily removed templates to make replicas of solid objects can be dated back to ancient Greece, where hollow bronze statues were cast by the "cire perdue" or lost-wax method. In this method, easily manipulated wax was embedded between an external and an internal clay figures; the wax was then removed by heating and replaced by liquid bronze. After removing both the external and the internal molds, hollow bronze statues were cast. Presently, the templating strategy has been extensively applied to nanotubes, porous alumina and bacteria to make novel materials possessing interesting and useful properties, hard or even impossible to be made by usual methods. In this Chapter, we explore the templating chemistry strategy to make virtually any colloid with size distributions of 5%, and its corresponding colloidal crystals through a modern nanoscale lost-wax method.

Experimental Sections

Materials and Substrates. All solvents and chemicals are of reagent quality and used without further purification except for tetraethoxysilane (99%, Alfa) which is freshly vacuum distilled before use. 200 proof ethanol is obtained from Pharmaco Products and 29.6% ammonium hydroxide is purchased from Fisher. Ultrapure water (18.2 MΩcm\(^{-1}\)) is used directly from a Milli-Q water system. Titanium isopropoxide, zirconium \(n\)-propoxide and aluminum sec-butoxide are purchased from Alfa Aesar. Polyurethane (NOA-60) is purchased from Norland. Commercially available monomers are used: methyl methacrylate (Aldrich), styrene (Acros), allyl methacrylate (Aldrich).
2,2-Diethoxyacetophenone (Aldrich, 95%) is used as UV photoinitiator. Commercially available polystyrene (average $M_w \approx 230,000$, melt index 8.5, glass transition temperature $T_g \approx 94^\circ C$) and PMMA (average $M_w \approx 350,000$, glass transition temperature $T_g \approx 122^\circ C$) are obtained from Aldrich. Microslides ($75 \times 25 \times 1 \text{ mm}$, Fisher) are cut into two equal halves along the long sides and are used as substrates. Glass scintillation vials (20 mL, Fisher) are used as experimental cells.

**Instrumentation.** Scanning electron microscopy and Energy-Dispersive X-ray (EDX) analysis are carried out on a Philips XL30 ESEM. A CrC-100 sputtering system is used to sputter a thin layer (3-4 nm) of gold on samples before SEM analysis. Transmission electron microscopy is carried out on a JEOL 2010 operating at 200kV. Transmission spectra are obtained using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer. An Oriel model 60000 UV lamp (320 W) with 68806 basic power supply is used to initiate the polymerization. An Isotemp vacuum oven (Model 281A) is used to convert poly(p-phenylenevinylene) (PPV) precursor into fully conjugated PPV and decompose metallic oxalates into zero-valence metals.

**Colloidal Silica Synthesis and Colloidal Crystal Growth.** Monodisperse SiO$_2$ nanospheres are synthesized following the Stober-Fink-Bohn method.$^{18}$ Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviation smaller than 5% are obtained through strict control of the reaction conditions.$^{81}$ The methods described in our previous paper$^{68}$ are used to fabricate three-dimensionally ordered planar colloidal crystals with thickness ranging from one monolayer to 50 μm. Chapter 1 describes more details of the colloidal silica synthesis and the colloidal crystal growth.
Fabrication of Three-Dimensionally Ordered Macroporous Polymers. Macroporous poly(methyl methacrylate) (PMMA), poly(allyl methacrylate) (PAMA) and polystyrene are made by photopolymerizing monomers as described in our previous paper\textsuperscript{45} and in Chapter 3. 1\% (wt\%) 2,2-diethoxyacetophenone (Aldrich, 95\%) is used as UV photoinitiator. 0.2 mm Teflon spacers are used to separate the two microslides to from a strong self-standing macroporous polymers. For the polymer stretch experiments to make non-spherical colloids, commercially available polymers are directly used to make thick macroporous polymers (~4 mm thick) as described in Chapter 3.

Fabrication of Ceramic Colloidal Crystals. Titanium isopropoxide (70\% in 2-propanol), zirconium \textit{n}-propoxide (20\% in \textit{n}-propanol) and aluminum \textit{sec}-butoxide (50\% in 2-butanol) are used as precursors to deposit metallic oxides into the voids of the macroporous polymers. First, macroporous polymers are soaked in the precursor solutions until they became transparent due to the close refractive index match to the alcohol. Next, the films are removed and placed in ultra-pure water (Milli-Q, 18.2 MΩ cm\textsuperscript{-1}) for 8 hour followed by drying under nitrogen. As metal oxides begins to form, the film turns slightly hazy. After repeated exposure to the alkoxide solution, followed by immersion in water, the films ultimately become opaque. After filling the voids of the macroporous polymers with metal oxides, the polystyrene templates can be dissolved in organic solvents (toluene or 1,2-dichloroethane) and PMMA templates can be burned out by propane torch for 1 minute to release the colloidal crystals. The typical size of the synthesized colloidal crystal is several square millimeters. To make larger, stronger colloidal crystals for optical characterization, a transparent polyurethane backing thin film can be used to affix the colloidal crystals on glass slides by photo-polymerizing
NOA 60. To avoid the penetration of the polyurethane monomers into the voids of the hollow spheres, the monomers are pre-polymerized into very viscous glues. Then the colloidal crystals is glued onto polyurethane, which can then be quickly polymerized. After dissolving the polymer template in organic solvents, a robust colloidal crystal up to several square centimeters is formed.

**Preparation of Monodisperse Ceramic Colloids.** The colloids formed by the lost-wax technique are initially prepared as colloidal crystal films, which can then be fragmented into individual constituent particles by ultrasonication using a ultrasonic bath (Fisher, FS6). Brief treatments (half a minute in a 40 W ultrasonic bath) in solvents such as toluene and ethanol yield larger pieces of colloidal crystal fragments (several millimeters in size), which were ideal specimens for transmission electron microscopy studies of the array geometry. Longer treatments, up to thirty minutes, provided totally dispersed colloids. The impurities and agglomerated particles are precipitated in several minutes after the ultrasonication and can be easily removed. The colloidal dispersions will not precipitate in several days.

**Preparation of CdS and AgCl Colloidal Crystals and Their Corresponding Monodisperse Colloids.** Macroporous polymers membranes were soaked in 0.2 M Cd(NO₃)₂ aqueous solution (with 20% by volume ethanol) until they become transparent. Next, the films are removed and immersed in 0.2 M Na₂S aqueous solution (with 20% by volume ethanol) for 8 hour. After repeated exposure to the Cd(NO₃)₂ solution, followed by immersion in Na₂S solution, the films ultimately become yellowish for CdS and opaque for AgCl. The cycle of penetration and reaction can be repeated for several times to make solid or hollow CdS colloidal crystals with different shell thickness. The removal
of the macroporous polymers, the reinforcement of the colloidal crystals with polyurethane backing films and subsequently redispersion of the colloidal crystal films into monodisperse colloids are similar to the preparation of ceramics ones as described above.

**Preparation of Polymeric Colloidal Crystals.** A macroporous polystyrene film is placed onto a drop of NOA 60 (polyurethane precursor, Norland) on a glass slide. The precursor can then penetrate into the voids of the macroporous polymers in several seconds and the film becomes transparent due to the close index match. The precursor is polymerized by exposure to UV light (320 W) for several minutes. Afterwards the polystyrene film can be dissolved in toluene and an iridescent polyurethane film is formed on the glass slide. To make conductive polypyrrole colloidal crystals, the macroporous polystyrene membranes are first soaked in 20 ml 20% (v/v) pyrrole/ethanol solution for 1 minute. The films are then removed and immersed in 20 ml 0.05 M FeCl₃ aqueous solution for 12 hours. A thin polyurethane backing film is then applied to stick the polypyrrole colloidal crystals onto glass slides to strengthen them for SEM analysis.

To make conductive poly(p-phenylenevinylene) (PPV) colloidal crystal, a macroporous polystyrene membrane is laid down on the flat bottom of a polystyrene dish, which are subsequently filled with PPV precursor methanol solution. The preparation and purification procedures of the PPV precursor methanol solution are described in detail in Chapter 3. When methanol is totally evaporated in dark in about two days, the polystyrene membrane filled with PPV precursor is removed from the dish and heated in a vacuum oven at 80°C for 1 hour. The polystyrene template is then dissolved in toluene and the PPV film was heated to 350°C under vacuum for another 3 hours to form fully
conjugated PPV. The ultrasonication has not been tried to separate the polymeric colloidal crystals into monodisperse colloids.

**Preparation of Metallic Colloidal Crystals.** To form hollow sphere metallic colloidal crystals, we adapt the metal templating chemistry used to infiltrate opals developed by Stein et al. to make macroporous metals.\(^{82,83}\) As an example, we start by forming nickel oxalates in polystyrene templates by immersing the templates in 0.2 M nickel (II) acetate ethanol/water (v/v: 1/1) solutions and then 1 M oxalic acid ethanolic solutions. Nickel oxalate is formed on the inner walls of the voids of the macroporous polystyrene templates. The thickness of the nickel oxalate can be varied by changing the number of the immersion-reaction cycles. The polystyrene/oxalate composites are washed with Milli-Q water and then calcined in flowing nitrogen at 450°C for 10 hours. This treatment allows the polystyrene to be burned out and converts the nickel oxalate into metallic nickel as shown in Equation 5.1:

\[
\text{NiC}_2\text{O}_4 \rightarrow \text{Ni} + 2 \text{CO}_2 \tag{5.1}
\]

In the same way, metallic cobalt, copper, cadmium and lead hollow colloids can also be made.\(^{82,83}\)

Solid metallic colloidal crystals can be made by filling the macroporous polystyrene templates with pre-formed metallic nanoparticles. As an example, we fabricate solid gold colloidal crystals in polystyrene membranes. The thio-derivatised gold nanoparticles are synthesized according to Burst et al.\(^{84}\) and the synthetic details are described in Chapter 4. 0.2 g of totally dried gold nanocrystals is dissolved in 10 ml hexane and used as the filling solution. To fill the voids, a macroporous polystyrene membrane is laid down on the flat bottom of a polystyrene dish, which are subsequently
filled with the synthesized gold nanocrystal solution. When hexane is totally evaporated in several hours, the polystyrene membrane filled with gold nanocrystals is removed from the dish and stuck onto a glass slide using polyurethane. The polystyrene template is dissolved in toluene to release the colloidal crystal.

**Fabrication of Ellipsoidal Colloidal Crystals.** Figure 5.1 shows the schematic illustration of the metal frame used for stretching macroporous polymer films.

![Schematic illustration of the metal frame used for stretching macroporous polymer films.](image)

*Figure 5.1.* Schematic illustration of the metal frame used for stretching macroporous polymer films.

Macroporous polystyrene strips (4 × 1 × 0.4 cm) are clamped into the metal frame and filled with mineral oil. The frame is then put in an oven preheated to a temperature 20-30°C higher than the glass transition temperature ($T_g$) of the polymer for several minutes until the polymer is soft. For polystyrene ($T_g \approx 94°C$), we set the oven temperature at 110°C. Then the macroporous polymer film is stretched to a length corresponding to a preset draw ratio by varying the positions of the film stops in the oven. The film is then taken out of the oven and cooled down to room temperature, while still constrained in the frame. The mineral oil is removed using heptane wash for three times followed by a 200 proof ethanol wash. These deformed macroporous polymers can then be used as
templates to make ellipsoidal colloidal crystals by filling the voids using the same methods described before.

Characterization of the Templated Colloidal Crystals and Monodisperse Colloids. The templated colloidal crystals can be affixed to conductive carbon tape and prepared for scanning electron microscopy by sputtering a thin layer (3-4 nm) of gold onto the surface. A Philips XL30 ESEM has been used to evaluate the resulting materials. The samples are broken using a sharp razor blade and are tilted 30-40° to obtain the cross-sectional images. In-situ Energy-Dispersive X-ray (EDX) analysis on the same ESEM is used to evaluate the chemical compositions. For transmission electron microscopy, drops of a dilute dispersion of ultrasonicated colloids are deposited on Formvar-coated electron microscope grids. The latter are examined using a JEOL 2010 operating at 200kV.

The optical properties of hollow sphere titania films are evaluated by measuring their transmission spectra at normal incidence, using an Ocean Optics ST2000 fiber optic UV-Near-IR spectrometer. Titania hollow sphere colloidal crystals with different shell thickness are stuck on glass slides using polyurethane. Pure polyurethane film with the same thickness is used as reference.

Results and Discussions

Fabrication of Spherical Monodisperse Colloids and Their Colloidal Crystals by Lost-Wax Method. Existing strategies for preparing monodisperse colloids, and thus colloidal crystals, generally manipulate the complex chemistry of colloid formation and the vexing colloidal interactions. Only silica and some polymer colloids and
their corresponding colloidal crystals, however, can be routinely prepared in high quality. Our method leverages the high perfection of silica colloidal crystals, effectively replicating their size distribution and arrangement in many other materials through a modern nanoscale "cire perdue" (lost-wax) method. Figure 5.2 shows the scheme of the templating processes. First, silica colloidal single crystals are formed through a convective self-assembly method (Figure 5.2A) as described in Chapter 1 and our previous paper.68 Next, these thin-film arrays are used as templates to generate macroporous polymers containing spherical and ordered voids (Figure 5.2B) as described in Chapter 3 and our previous paper.45 A key feature of these macroporous polymers is the interconnectedness of their pores; scanning electron microscopy (inset of Figure 5.2B) shows that each void is connected to its neighbors through smaller windows whose mean dimension can be precisely controlled through the viscosity of the starting monomer.45 Such microstructure allows these macroporous polymers to be filled with different liquid precursor solutions in a second templating process. Further chemical or photochemical reactions then solidify the precursors and fill the cavities. The host macroporous polymer can be removed by dissolution in an appropriate solvent, or by heating, leaving behind an array of colloids which retain the initial silica template geometry (Figure 5.2C).
**Figure 5.2.** Scanning electron microscopy (SEM) images of colloidal crystal preparation processes by lost-wax method. (A) SiO$_2$ colloidal crystal template. (B) Macroporous polystyrene template replicated from above silica template. The inset shows a higher magnification image ($\times$ 50,000) of the interconnecting inner pores between the voids. (C) Solid titania colloidal crystal replica from a PMMA template after burning out the template by a propane torch. The inset shows a Fourier transform of a 40×40 $\mu$m$^2$ region in the (111) plane.
A wide variety of materials including ceramic, polymer, semiconductor and metal colloids and their colloidal crystals can be made by this method (Table 5.1). To make the table, over 200 particles are measured in SEM images to arrive at the values reported. Macroporous polystyrene samples with void diameter $333 \pm 14.3$ nm templated from silica colloidal crystals with diameter $336 \pm 12.4$ nm are used to make all spheres in the middle column; while macroporous PMMA samples with void diameter $288 \pm 13.8$ nm templated from silica colloidal crystals with diameter $294 \pm 13.8$ nm were used to make all spheres in the right column. For ceramic colloids, we use the hydrolysis and condensation reactions of metallic alkoxides with water to deposit metallic oxides into the voids of the macroporous polymers as shown in Equation 5.2 and 5.3:

**Hydrolysis:** \[ M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH \] \[ [5.2] \]

**Condensation:** \[ M(OH)_4 + M(OH)_4 \rightarrow (HO)_3M-O-M(OH)_3 + H_2O \] \[ [5.3] \]

where M can be Ti, Zr, Al, Si, W, Fe, Sb, or a Zr/Y mixture, R can be methyl, ethyl, isopropyl, n-propyl, sec-butyl or n-butyl group. After repeated exposure to the alkoxide solution, followed by immersion in water, the macroporous polymer films ultimately become opaque. The polymeric templates can then be removed by dissolving in appropriate organic solvents for polystyrene or by burning out using a propane torch (Turner) for 1 minute for PMMA. The average diameters of colloids templated from polystyrene keep those of the original silica templates, while those from PMMA templates show roughly a 10% reduction in dimension which is reasonable given the shrinkage that occurs during the template removal process.\(^{41,44,52}\) (see Table 1)
Table 5.1. Size and size distribution of colloids synthesized by the templating process.

<table>
<thead>
<tr>
<th></th>
<th>Spheres Made from Macroporous Polystyrene Templates (nm)</th>
<th>Spheres Made from Macroporous PMMA Templates (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>325.0 (5.2%), hollow</td>
<td>267.8 (4.8%), solid</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>327.1 (5.1%), hollow</td>
<td>271.3 (5.3%), solid</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>327.3 (4.7%), hollow</td>
<td>273.7 (5.5%), solid</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>322.0 (4.8%), hollow</td>
<td>N/A</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>319.7 (4.3), solid</td>
<td>N/A</td>
</tr>
<tr>
<td>PPV</td>
<td>310.5 (5.6%), solid</td>
<td>N/A</td>
</tr>
<tr>
<td>CdS</td>
<td>323.7 (6.3%), hollow</td>
<td>269.6 (6.1%), solid</td>
</tr>
<tr>
<td>AgCl</td>
<td>325.2 (5.7%), hollow</td>
<td>270.9 (5.2%), solid</td>
</tr>
<tr>
<td>Au</td>
<td>319.7 (5.3%), solid</td>
<td>N/A</td>
</tr>
<tr>
<td>Ni</td>
<td>306.6 (5.9%), hollow</td>
<td>N/A</td>
</tr>
</tbody>
</table>

We discovered that in addition to hollow forms, solid spheres can also be grown within the voids of the macroporous polymer by manipulating the adhesion between the ceramic colloids and the host polymer. When macroporous PMMA is used as a template, the ceramic layer pulls away from the host polymer after condensation and forms solid spheres smaller than the cavities (Figure 5.3A). The observed incomplete filling of the voids is reasonable considering the use of diluted metal alkoxides and the large shrinkage (20~30%) of alkoxide hydrolysis and condensation to form ceramics. A similar reduction in ceramic particle size was observed in a single-step emulsion template method. Complete filling of the voids is accomplished by repeated immersion/filling cycles. The
PMMA template can be burned out using a propane torch in air, leaving an array of solid ceramic spheres as shown in Figure 5.4A. In contrast, when templated against polystyrene, the same ceramic adheres strongly to the polymer walls (Figure 5.3B), which results in the formation of an array of hollow spheres upon template removal (see Figure 5.4B). The thickness of the ceramic hollow sphere walls can be increased by re-exposing an oxide-polymer composite of the type shown in Figure 5.3B to more metal alkoxide and water as shown by the transmission electron microscopy (TEM) images in Figure 5.5. The hollow shells grow until the interconnecting voids (~60 nm diameter) are completely blocked. By this way, the shell thickness of these templated hollow spheres can be tuned by varying the number of coatings as shown in Figure 5.6. By starting with a macroporous polymer with larger interconnecting voids (~120 nm), much thicker shells (over 100 nm) can be formed.

We have found that other inorganic materials, such as CdS and AgCl also show a tendency to adhere strongly to polystyrene, and not to PMMA. Figure 5.7 shows a SEM top-view image of a hollow CdS colloidal crystal templated from polystyrene. It is likely that this difference in adhesion arises from the distinct surface interactions possible at the inorganic-polymer interface. The overall adhesion energy, $E_{ad}$, can be expressed as:

$$E_{ad} = E_{polymer} + E_{ceramic} - \gamma_{polymer-ceramic}$$  \[5.4\]

where $E_{polymer}$ and $E_{ceramic}$ are the surface free energies for polymer and ceramic respectively. Since PMMA and polystyrene have similar surface free energies and for the same ceramic, $E_{ceramic}$ is the same, the difference between the two polymers must lie in the interfacial free energy. So we believe that the interfacial free energy between the polymer and ceramic is the main contribution to their apparently different adhesion
properties. We speculate that the polystyrene will function as a strong \( \pi \)-donating ligand with the metal centers in the inorganic materials, leading to an increased adhesion between the growing colloids and polystyrene template. \(^86\)

**Figure 5.3.** SEM images of two growth mechanisms of titania formed from sol-gel method within the voids of polymer templates cast from 332 nm silica spheres. (A) TiO\(_2\) solid particles (178 ± 9.8 nm) pull away from the PMMA template (coated twice). (B) TiO\(_2\) hollow particles (37.9 ± 4.5 nm shell thickness) adhere strongly to the polystyrene template surface (coated nine times).
Figure 5.4. SEM images of colloidal crystals made by lost-wax method. (A) Solid TiO$_2$ colloidal crystal replicated from PMMA template after coating seven times. (B) A hollow titania colloidal crystal replica (coated nine times) obtained by dissolving the polystyrene template in toluene.
Figure 5.5. Transmission electron microscopy (TEM) images of hollow titania colloidal crystals of different shell thickness by varying the number of coatings. (A) $10.5 \pm 0.6$ nm shell thickness, 1 time coating. (B) $27.4 \pm 2.3$ nm shell thickness, 5 times coating.
Figure 5.6. The relationship between the shell thickness of the hollow spheres templated from macroporous polystyrene with the number of coatings.

Figure 5.7. SEM top-view image of a hollow CdS colloidal crystal templated from macroporous polystyrene.
As many emerging applications for colloidal materials require particle morphologies quite different from a single-component solid sphere, the flexibility of this approach is a real advantage. One form we explored is the hollow colloidal capsule for use in drug delivery\textsuperscript{87,88} and enzyme immobilization.\textsuperscript{89} We chose polypyrrole (Ppy) as a target material because of its possible use in drug delivery applications.\textsuperscript{90,91} Successive dipping of a macroporous polystyrene template in a 20\% (\textit{v/v}) pyrrole ethanol solution and a 0.05 M FeCl\textsubscript{3} aqueous solution formed conductive polypyrrole (see Equation 5.4) capsules arrays as shown in Figure 5.8A.

\[ n \begin{array}{c} \text{N} \\ \text{H} \end{array} + 2n \text{FeCl}_3 \rightarrow \left( \begin{array}{c} \text{N} \\ \text{H} \end{array} \right)_n + 2n \text{FeCl}_2 + 2n \text{HCl} \quad [5.4] \]

When the sample is compressed prior to imaging, the colloids collapse into irregular shapes, much like deflated soccer balls as shown in Figure 5.8B. Existing methods for forming polymer capsules rely on layer-by-layer assembly of polyelectrolytes \textsuperscript{92}, or the formation of block co-polymer assemblies \textsuperscript{93}, which necessarily limit the choice of polymer materials. In our method, the only constraint placed on the choice of material is that its polymerization must occur under conditions which do not destroy the host template.
Figure 5.8. SEM images of a hollow polypyrrole colloidal crystal replicated from a polystyrene template. (A) Cross-section view along a crack. (B) The same sample after being compressed.
Metallic nanospheres and nanoshells are also a colloidal target of great interest due to their interesting and valuable optical and physical properties 94-97. They are notoriously difficult to form in the 50 to 500 nanometer range in pure form by standard chemical methods. We fashioned them in a manner similar to that used for polymers and inorganics by adapting the metal templating chemistry used to infiltrate opals developed by Yan and Stein et al.82,83 We start by forming metallic oxalates in polystyrene templates using metallic acetate ethanol/water (v/v: 1/1) solutions as precursors and oxalic acid ethanolic solutions as precipitating agents. The polystyrene/oxalate composites are then calcined to form zero-valence metals. Since the metallic oxalates adhere strongly to the polymer walls as ceramics do, hollow metallic colloidal crystals are fabricated as shown in Figure 5.9. In-situ Energy-Dispersive X-ray (EDX) analysis indicates that the metals are quite pure (over 95% atom%). In the same way, metallic cobalt, copper, cadmium and lead hollow colloids can also be made.

**Figure 5.9.** Top-view SEM of a hollow nickel colloidal crystal replicated from a polystyrene template. Several broken colloids are clearly seen in the image. The inset shows a Fourier transform of a 40×40 μm² region in the (111) plane.
Another valuable colloidal morphology accessible with this strategy is the formation of core/shell composite colloids. In such a geometry it is possible to design a robust outer shell to chemically and physically protect a more fragile interior colloid which might possess special optical or magnetic properties. Figure 5.10 shows an example from our method of a zirconia/alumina hollow core-shell colloid made by successive deposition of alumina and then zirconia via alkoxide hydrolysis within a polystyrene template. Since zirconia has a higher electron density than alumina it appears darker in the electron microscopy image. *In-situ* Energy-Dispersive X-ray (EDX) and microprobe analysis indicate the expected stoichiometric proportions of the materials. This result illustrates that encapsulation of materials on the inner surface of the hollow spheres is feasible. Furthermore, core-shell structures formed by successive depositions can be generalized to the solid spheres.

![TEM image of core-shell structure](image)

**Figure 5.10.** TEM image of the core-shell structure of a hollow zirconia/alumina colloid formed from successive deposition of alumina and then zirconia (each coated twice) on the surface of a polystyrene template.
The macroporous polymer templates can also be completely filled physically rather than chemically, where they act as a three-dimensional analog of the "soft lithography" elastomeric stamps used to make two-dimensional patterns. We have made solid poly(\(p\)-phenylenevinylene) (PPV) and Au colloidal crystals by filling the macroporous polystyrene films with PPV precursor/methanol solution or gold nanocrystals/hexane solution. The solvents were slowly evaporated to deposit solids deep inside the pores and the templates were removed by dissolution in toluene. Figure 5.11 shows a SEM cross-section view of a PPV sample made by this method. The general nature of this physical filling allows one to make solid colloidal crystals from a large number of other materials, including many available nanocrystals.

Figure 5.11. SEM cross-section view of a PPV sample made by three-dimensional soft lithography.
The colloids formed by the lost-wax technique are initially prepared as solid films. We investigated whether the particles could be isolated as individual colloids in solution. Ultrasonication is a well established method for breaking up colloidal aggregates in solution,\(^{101}\) and we found that it was also successful at fragmenting these colloidal films. Brief treatments (half a minute in a 40 W ultrasonic bath) in solvents such as toluene yielded larger pieces of colloidal crystal fragments (several millimeters in size), which were ideal specimens for transmission electron microscopy studies of the array geometry (see Figure 5.5 and 5.12). Longer treatments, up to thirty minutes, provided dispersed material of the type shown in Figure 5.13. One interesting feature of the dispersed colloids was the uniformity of the surfaces (Figure 5.13). While the geometry of the macroporous host contains windows between the spherical voids, colloidal material does not appear to template these channels at any significant density. We attribute this to the relative size of the windows, which is only 10-20% of the void size, and to the colloidal shrinkage induced during the condensation or polymerization reactions.\(^{85}\)

![Figure 5.12. TEM image of a fragment of a hollow titania colloidal crystal after brief ultrasonic treatment.](image)
Figure 5.13. Transmission electron microscopy (TEM) images of monodisperse particles made by long time ultrasonic treatment of the templated colloidal crystal films. (A) Solid titania colloids with 262 ± 5 nm diameter replicated from PMMA template after coating seven times. (B) Hollow titania colloids with 267 ± 14 nm diameter and 31.4 ± 2.3 nm shell thickness replicated from polystyrene templates after coating seven times;
The primary advantage of this approach to colloidal synthesis is that uniformity control is completely affected by the template, thus transferring this burden to the original silica colloids for which high quality samples are routinely available. To evaluate the effectiveness of this templating process we measured the final particle size and size distribution using scanning electron microscopy images such as the one shown in Figure 5.9. These are compared to the characteristics of the starting silica colloids and macroporous polymer voids in Table 1. Size distributions remain remarkably narrow after the templating steps; clearly, the final colloids faithfully reproduce the uniformity of the silica colloids. While there are chemical methods for producing some of these colloids with relatively narrow size distributions (around 10%),9,102 this templating approach provides a strategy for creating a wide range of highly monodisperse colloids (around 5%). While we demonstrated this method for only two sphere sizes (336 nm and 294 nm), we note that mesoporous polymers can be formed from silica spheres with diameters as small as 30 nanometers.47 There is no apparent reason that these simple chemical and physical filling techniques used for these large spheres could not be extended to templates with smaller void sizes.

Except for ultrasonication in appropriate solvents, the templated colloidal crystals are remarkably robust, high-quality materials. The long-range order of the crystals is apparent in scanning electron microscopy (SEM) image, such as those in Figure 5.7 and 5.9. A Fast-Fourier transform (FFT) of the image provides a measure of order in the (111) plane (see inset of Figure 5.9). Though defects such as cracks and point defects can be observed, the single crystalline nature of the starting silica colloidal crystals is retained during the templating process. The ordering perpendicular to the close-packed (111) axis
is best visualized in cross-sectional images; an example of such data for an alumina solid sphere sample is shown in Figure 5.14. The cross-sectional images show that these samples are films, not monoliths, and that their (111) axis is perpendicular to the underlying glass substrate. The film thickness can be precisely controlled from single monolayers to over 100 layers due to the faithful replication of the starting silica colloidal crystal. In addition, we can directly observe the relative positions of the crystallization planes from transmission electron microscopy images of hollow sphere colloidal crystals (Figure 5.12) by consecutively focusing on stacked crystallization planes. We found in several images of 4-6 layers that the spheres are stacked in an ABCABC pattern consistent with a face-centered cubic (FCC) structure. While such microscopic evidence is not an accurate measure of the average stacking in an entire crystal, we note that the FCC packing is expected to be more stable than hexagonal close-packing (HCP) even for hard spheres.

![Cross-section SEM image of a solid Al₂O₃ colloidal crystal replicated from PMMA template after coating seven times.](image)
Optical Properties of the Hollow Sphere Colloidal Crystals with Controlled Shell Thickness. In addition to direct imaging we also characterized our double-templated colloidal crystal films using optical transmission. These measurements are relevant because one of the emerging applications for colloidal crystals is their use in the formation of visibly active photonic band gap materials. Figure 5.15 shows the normal-incidence transmission spectra of the starting colloidal crystal film, the macroporous polymer film formed from it, and two examples of films of ceramic hollow spheres. The presence of a well-defined stop band in all samples confirms that the high degree of order evident in the silica colloidal crystals is preserved throughout the double-template process.\(^{104}\) As noted previously, we cannot rule out stacking faults in these materials; however, both the hcp and fcc structures have the same \((111)\) d-spacing and packing fraction so scattering along this direction is relatively insensitive to this particular defect.

The peak positions of the stop bands are quite sensitive to the average index of a material and the colloids' diameter. In all four spectra, the arrows indicate the expected position of the optical stop band, determined using Bragg's Law at normal incidence. For the two samples of hollow spheres, the average index \(n_{\text{ave}}\) is determined by treating the hollow spheres as solid spheres with an effective index given by the volume-weighted average, computed using the known shell thickness. For both TiO\(_2\) and ZrO\(_2\), the refractive indices of the bulk crystalline media (\(n_{\text{titania}} = 2.49\), \(n_{\text{zirconia}} = 2.13\)) have been used. Since the shells are amorphous and probably not densified, these values represent an upper limit on the indices of the materials, and thus the estimated spectral positions represent the longest wavelengths one could obtain from this calculation. In (A) and (B), Bragg's Law
is reasonably accurate, but the hollow spheres evidently require a more sophisticated treatment.

Figure 5.15. Normal-incidence visible/IR transmission spectra of four nanostructured films. (A) Crystal of silica colloids, of 342 nm diameter. (B) Macroporous polystyrene film formed using the sample of (A) as a template. (C) Crystal of hollow titania spheres, formed in the pores of the polystyrene film of (B), with a shell thickness of 16±2 nm. (D) Crystal of hollow zirconia spheres, formed in the pores of the polystyrene film of (B), with a shell thickness of 3±1 nm.
A central goal of the community using colloidal systems has been the generation of samples with increasingly stronger photonic properties, with the ultimate aim of forming a material possessing a fully three-dimensional photonic band gap. While the materials shown here do not possess such a property, they do show strong photonic behavior comparable to that observed in macroporous high-index ceramics. Prior experimental and theoretical studies of colloidal crystal optics have used the fractional stop band width, $\Delta \omega / \omega$, as a metric for the size of their photonic band gap: broad peaks occur when the band gap along that axis is large.\textsuperscript{105,106} For hollow titania with a thick shell, a relative width of 11% is observed for its stop band. This is comparable to the width reported for macroporous titania,\textsuperscript{41,50} suggesting that hollow sphere colloidal crystals may provide a valuable morphology for fabricating photonic band gap materials with larger gaps. This is not surprising, as recent calculations suggest that incompletely filled macroporous materials, similar to hollow spheres, can exhibit enhanced photonic band gaps under certain conditions.\textsuperscript{105,107} In addition, our method allows for accurate control over both the shell thickness (which is analogous to the degree of infiltration) and the overlap between spheres (analogous to the sphere connectivity), because of the existence of the interconnecting windows which prohibit the air spheres from being closer to each other than one sphere diameter. These are the two parameters identified by Busch et al.\textsuperscript{105} as key factors in controlling the width of the stop band.

To demonstrate that the lost-wax method provides the ability to tune the band gap using these new parameters, we have studied the optical transmission spectra of four titania hollow sphere colloidal crystals with different shell thickness as shown in Figure 5.16. There is an evident red-shift of the stop band as the shell thickness is increased.
This is phenomenologically consistent with Bragg's law at normal incidence. As the shell thickness is increased, the average index of the film also increases, leading to a red-shift. This simple scalar theory, using an effective medium approximation, has been shown to be reasonably accurate for propagation along high symmetry axes. The dashed line in Figure 5.17A shows the prediction of Bragg's law, assuming that the titania matrix has a refractive index of 2.

**Figure 5.16.** Transmission spectra of titania hollow spheres for increasing shell thickness. The band gap develops along the (111) direction between the 2\textsuperscript{nd} and 3\textsuperscript{rd} bands. The average sphere diameter (280 nm) and the number of layers (~15) were fixed. The stop band is red shifted as the shell thickness increases.
Figure 5.17. Transmission spectra analysis of the partial gap along the (111) direction. (A) Central frequency $\omega_0$ of the stop band as a function of the shell thickness. The black squares are the experimental data points, the dashed line is the prediction using a simple Bragg's law analysis and the solid line is the prediction from a full vector calculation. (B) Relative gap as a function of the shell thickness. There is an optimal shell thickness to maximize the gap.

In order to explain the bandwidths, we must resort to a more sophisticated theoretical approach. We calculate the band structure for the hollow sphere system using a full vector numerical technique from which both the spectral position and width of the stop band can be extracted. This method uses a frequency-domain iterative approach to perform a direct computation of the eigenstates and eigenvalues of Maxwell's equations using a plane wave basis. The solid lines in Figure 5.17 show the results of these
calculations. We note that, because both the shell thickness and the sphere overlap can be determined from electron microscopy, these are not adjustable parameters in the simulations. The only unknown parameter is the refractive index of the titania shells; it is known that the hydrolysis reactions used to form these samples produce oxides with lower indices than those of the bulk materials.\textsuperscript{110-112} As with the Bragg’s law calculation mentioned above, the simulations shown in Figure 5.17 assume a refractive index of 2 for the shell material, consistent with previous reports.\textsuperscript{112} The agreement between the data and these simulations is excellent, particularly for the fractional band widths.

**Fabrication of Ellipsoidal Colloidal Crystals.** As the sculptors of ancient Greece knew, the lost-wax technique allows for an incredible diversity of forms to be produced from a single starting object. Following their example, we investigated whether colloidal shape could be manipulated during the templating process. Of particular interest was the production of non-spherical colloids. They may offer advantages over their spherical counterparts in applications that require periodic structures with lower symmetries.\textsuperscript{19} In addition, monodisperse ellipsoidal latex colloids have been introduced as a potential model for rigid rod systems, such as liquid crystal polymers and biopolymers.\textsuperscript{113} Methods for preparing inorganic, polymeric and metallic colloidal cubes, ellipsoids, and rods have been reported for specific materials,\textsuperscript{9,113,114} but sample homogeneity is poor and a general methodology has not yet been developed.

Our method exploits the pliability of the macroporous polymer templates at high temperatures. When a macroporous polymer film is heated above its glass transition temperature ($T_g$), it becomes a rubber and can be stretched by an uniform uniaxial or
biaxial force. The draw ratio, $D$, characterizes the magnitude of this extension and for one
dimensional stretching is defined as the ratio of the extended length to the starting length.
To avoid collapse of the voids during the heating, we fill the pores with mineral oil prior
heating. The mineral oil can be easily moved by a heptane wash afterwards. If the film is
then quickly cooled down below $T_g$, while still constrained in the deformed state, the
shape of the stretched voids, oblate for a two dimensional extension and ellipsoidal for a
one dimensional extension, is fixed into the glassy, inflexible polymer. These non-
spherical voids can be replicated into many different materials using the same methods
described before. SEM images in Figure 5.18 show top-views of two hollow ellipsoidal
titania colloidal crystals with different axial ratios ($\rho$) templated from the same
macroporous polystyrene ($T_g = 92.1^\circ$C). The ellipsoidal shapes of the colloids and the
long-range order in the (111) plane are confirmed by the elongated hexagonal patterns of
the FFTs as shown in the insets of Figure 5.18A and 5.18B. We measured the lengths of
both the long axis and the short axis of these ellipsoidal colloids made with differing
draw ratios ($D_A = 1.3$ and $D_B = 1.7$). The sample in Figure 5.18A has a $489 \pm 27$ nm long
axis, a $333 \pm 18$ nm short axis, and an axial ratio of 1.47; the sample in Figure 5.18B has
a $624 \pm 43$ nm long axis, a $281 \pm 14$ nm short axis and an axial ratio of 2.22.
Figure 5.18. Top-view SEM images of ellipsoidal colloidal crystals. (A) A hollow titania sample (four times coating) templated from a macroporous polystyrene (429 ± 16 nm diameter voids). Draw ratio $D = 1.3$. The inset shows a Fourier transform of a 40×40 μm$^2$ region in the (111) plane. (B) A hollow titania sample (four times coating) templated from the same macroporous polystyrene sample. $D = 1.7$. The inset shows a Fourier transform of a 40×40 μm$^2$ region in the (111) plane.
It is possible to achieve a high degree of control over the aspect ratio of the resulting colloids using this method. We can predict the axial ratios ($p$) of ellipsoidal samples from their corresponding draw ratios ($D$) by assuming the volume of the voids does not change during the stretch; this assumption is reasonable since the voids are filled with mineral oil which is not likely to undergo a significant change in density as a result of the modest forces during extension. The ellipse major and minor axes are related to the starting sphere diameter by,

$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi a^2 b$$  \[5.6\]

where $r$ is the radius of the spherical voids, $a$ and $b$ are the semi-axes of the ellipsoidal voids. In addition, the long semi-axis can be related to the draw ratio by,

$$b = D \times r$$  \[5.7\]

where $D$ is the draw ratio. Replace this in the above equation, we get

$$a = D^{1/2} \times r$$  \[5.8\]

Thus the axial ratio, $p$, is

$$p = \frac{b}{a} = D^{3/2}$$  \[5.9\]

The measured axial ratios of four ellipsoidal samples with differing draw ratios shown in Figure 5.19 agree well with this simple model. A similar result has also been observed in a polystyrene latex/poly(vinyl alcohol) system. Axial ratios larger than 5.0 are not feasible as the polymer begins to tear as a result of the tensile force; the use of more flexible polymers such as poly(dimethylsiloxane) (PDMS) may alleviate this issue.
The ordering perpendicular to the close-packed (111) axis of these elliptical colloidal crystals is apparent in the cross-sectional image in Figure 5.20A (same sample as Figure 5.18B). The sample templated from polystyrene is hollow as shown by the broken colloids in Figure 5.20A and further confirmed by the TEM image in Figure 5.20B. The ellipsoids are monodisperse with a uniform shell thickness. This indicates that the heating and stretching process does not change the surface properties of the polymer substantially, so all the morphologies and materials developed for the non-stretched templates can be extended to these non-spherical examples. Ellipsoidal colloidal crystals with high refractive index may pave the way for building new photonic crystals with superior optical properties, since geometric anisotropy has been shown to widen the photonic band gap of colloidal materials.116-119
Figure 5.20. Electron microscopy images of ellipsoidal colloidal crystals. (A) SEM cross-sectional view of a hollow titania sample. (B) TEM image of the same sample.
Conclusions

In this chapter we describe a modern nanoscale "cire perdue" (lost-wax) method for forming colloids with size distributions around 5%, and their corresponding colloidal crystals. We form our colloids by templating inside the cavities of a macroporous polymer which itself is a template of a silica colloidal crystal. Freed from the constraints of solution chemistry, we are able to generate a wide variety of highly monodisperse inorganic, polymeric and metallic solid and core-shell colloids, as well as hollow colloids with controllable shell thickness. Moreover, our method results in the direct formation of a colloidal crystal. Such crystals traditionally have been formed via a lengthy sedimentation process which is ill-suited to crystallizing dense colloids. Finally, our reliance on a pliable polymer template permits control over colloidal shape. We demonstrate this by forming crystals of elliptical particles with precisely controlled aspect ratios. While there are pre-existing routes for some of the colloidal structures presented, no single approach provides such a general strategy for forming new colloidal architectures. In addition, many of these colloidal crystals have never before been formed due to the difficulty with chemical preparation of highly uniform particles. This technique extends significantly the selection of accessible nanoparticle forms and colloidal crystals to include nearly every major class of functional materials. Such systems are of scientific interest and may find applications in areas ranging from photonic crystals to pharmaceuticals.
References


Appendix A

Publications


