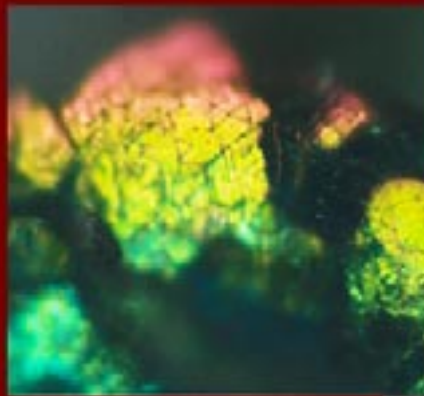# Inverse Opal Photonic Crystals
A Laboratory Guide

Rick Schroden
University of Minnesota

Nagalingam Balakrishnan
United Tribes Technical College

A University of Minnesota
Materials Research Science
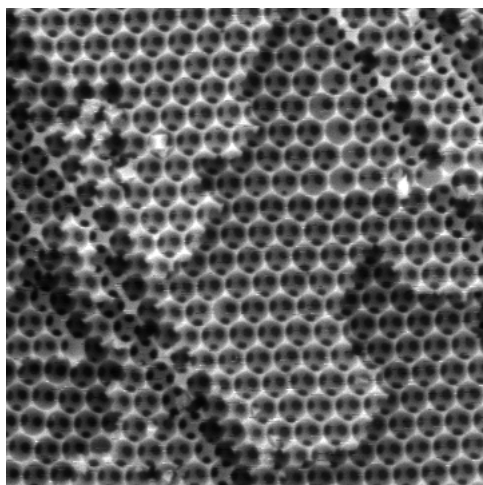and Engineering Center Publication

Inverse Opal Photonic Crystals

A Laboratory Guide

Authors
Rick C. Schroden
Nagalingam Balakrishnan

Contributing Authors
Andreas Stein
Michael D. Ward

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A Laboratory Guide

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ABOUT THE AUTHORS

Rick C. Schroden is a graduate student in the Chemistry Department at the University of Minnesota, advised by Professor Andreas Stein. He received his B.S. degree in Chemistry in 1997 from St. Cloud State University. His research interests include the design and analysis of porous materials for catalysis, optics, photonics, and sorption.

Nagalingam Balakrishnan is a science and mathematics instructor at the United Tribes Technical College in Bismarck, North Dakota. He earned his B. Sc. degree in Chemistry and Mathematics in 1983 from the University of Jaffna, Sri Lanka and his Ph.D. in Chemistry in 1992 from North Dakota State University. Dr. Balakrishnan currently teaches a range of courses at United Tribes, including chemistry, physical science, algebra, and precalculus. He has been the recipient of National Science Foundation grants for math and science enrichment in the American Indian Community.

Contributing Authors

Andreas Stein is an Associate Professor of Chemistry at the University of Minnesota. He received his B.Sc. in Chemistry in 1986 from the University of Calgary and his Ph.D. in Physical chemistry in 1991 from the University of Toronto. His research group focuses on controlling the composition, architecture and surface properties of inorganic and hybrid porous materials.

Michael D. Ward is a Professor of Chemical Engineering and Materials Science at the University of Minnesota and the Director of the University of Minnesota Materials Research Science and Engineering Center. He received his B.Sc. in Chemistry in 1977 from the William Paterson College of New Jersey and his Ph.D. in Chemistry in 1981 from the Princeton University. His research interests revolve around crystal growth and design.

FOREWARD

This laboratory guide was conceived during the summer of Y2001 at the University of Minnesota Materials Research Science and Engineering Center (UMN MRSEC) by Nagalingam Balakrishnan, a faculty member of the United Tribes Technical College who participated in the UMN MRSEC summer research program with his student Anna Gopher. This team worked in the research group of Professor Andreas Stein in the Department of Chemistry of UMN, studying the synthesis of "inverse opals," wherein uniformly sized polymer spheres are used as templates for sol-gel condensation reactions to produce inorganic solid replicas with uniformly spaced macropores. These materials are particularly intriguing because the uniform spacing of the macropores and the large periodicities result in peculiar optical properties that prevent the transmission of specific wavelengths of light. They are crystals in every sense of the word, but with the crystal lattice defined by the macropores. One glance at these crystals reveals light refraction identical to that observed in natural opals, which are simply crystals of uniformly spaced silica spheres. This laboratory guide has been prepared with the intention of teaching specific laboratory techniques – emulsion polymerization, templated sol-gel condensation, sintering, and optical measurements – to undergraduate students, and possibly high school students. We believe that the deep appreciation of jewelry and other artifacts, including opals, by Native American communities makes this a particularly attractive laboratory module for science instruction in tribal colleges.

Special thanks are due Dr. Frank Snowden, the Associate Direction of the UMN Education and Human Resources program, for his coordination of the outreach activities that led to this guide. This guide would not have been possible without the generous support of the National Science Foundation, which provided funding for the UMN MRSEC and its summer research programs for external participants.

Michael D. Ward
Director, UMN MRSEC

Table of Contents

Overview

This laboratory manual is designed to guide instructors and students in the preparation of inverse opal materials from beginning to end, including setup of equipment, preparation of polymer sphere templates, sol-gel templating to produce inverse opals, and study of optical properties. The best practices for successful results are given for each step, along with ordering information for specialized equipment. This lab exercise is recommended as a three-part experiment: Week 1 - synthesize the polymer sphere templates; Week 2 - synthesize the inverse opals; Week 3 - explore the optical properties. Alternatively, the lab exercise can be organized as a two-part experiment if the polymer templates are prepared in advance by either a student group or the instructor.

1. Introduction

A. Opals

Opals are among the most colorful of all gems despite being composed primarily of silica, a colorless solid with the chemical formula SiO_2 (opals have the same chemical composition as window glass and quartz). Their name comes from the Latin word *opalus* meaning "to see a change of color." They exhibit a play of color (often called opalescence), which consists of iridescent color flashes that

Figure 1. Photographs of opals displaying rainbows of colors that change as the angle of observation changes.

change with the angle at which they are viewed (Figure 1). The effect is similar to the rainbow of colors observed on a soap bubble, only much more dramatic. The origin of iridescence in opals comes from an ordered microstructure of closely packed silica spheres, which causes light to diffract from the planes of spheres. Since the size of these silica spheres is on the order of hundreds of nanometers, the wavelength of the diffracted light is also on the order of hundreds of nanometers. This range of wavelengths falls within the visible region of light, spanning approximately 380 to 750 nanometers. Visible wavelengths are those that can be detected by our eyes, and they cover only a small portion of the electromagnetic spectrum, which also includes gamma-rays, X-rays, ultraviolet, infrared, microwaves, and radio waves (Figure 2).

Diffraction of light from opals can cause flashes of any color of the rainbow, with the diameter and spacing of the silica spheres affecting the observed color. Opals made of smaller spheres tend to display the violets and blues (which have shorter wavelengths), while those made of larger spheres tend to display the reds (which have longer wavelengths). The more uniform the silica spheres with respect to size and arrangement, the more intense and defined the color.
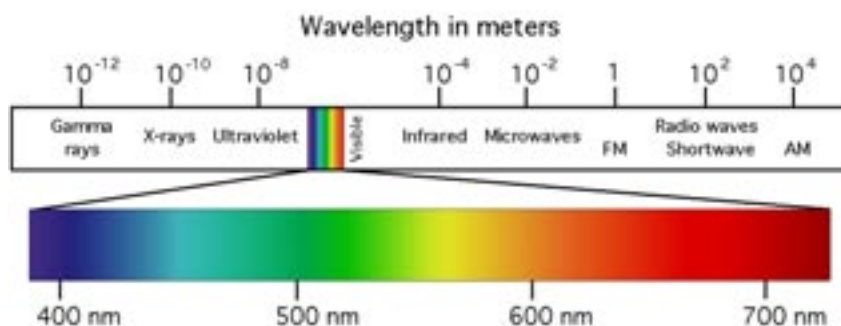
Figure 2. Classification of the wavelengths of radiation in the electromagnetic spectrum. The small range of wavelengths that can be detected by our sense of sight is called visible light. The bar at the bottom illustrates an approximate distribution of visible wavelengths.

B. Polymerization

A polymer is a large molecule consisting of many repeating chemical units, called monomers. Polymers are formed by the process of polymerization, in which many monomer molecules react to form very large molecules. Polymers generally are formed in two ways: step-growth polymerization or chain-growth polymerization. Step-growth polymerization involves the stepwise addition of monomers with two functional groups. Each reaction is essentially independent of the preceding one, and a polymer is formed simply because the monomers undergo reactions at more than one functional group. This makes step-growth formation of high molecular weight polymers difficult, and requires high-yield reactions to produce large polymers. By comparison, chain-growth polymerization involves the sequential addition of monomers to the end of an active polymer chain. In each case a reactive particle (such as a free radical, cation, or anion) produces another reactive particle, preserving the reactivity of the chain. As a result, chain-growth polymerizations allow the rapid preparation of very high molecular weight polymers.

The first part of the lab exercise involves the preparation of poly(methyl methacrylate) (PMMA) by a free radical chain-growth polymerization. PMMA is sold commercially under familiar trade names such as Plexiglas® and Lucite®. In this lab procedure, uniformly sized PMMA spheres will be prepared by the polymerization of methyl methacrylate (MMA) in water. Since MMA (which is an oily liquid) is not soluble in water, it must by polymerized by a process referred to as emulsion polymerization. An emulsion is a suspension of oil drops in water.

There are three stages in chain-growth polymerizations: initiation, propagation, and termination. These stages are illustrated in Figure 3 for the synthesis of PMMA that will be performed in this lab exercise. To begin the polymerization it is necessary to have an initiator, which is a molecule capable of forming a reactive particle. Azo-compounds, which decompose upon heating to produce two organic radicals and nitrogen gas, are commonly used initiators. The initiator used in this experiment is the azo-initiator 2,2'-azobis(2-methylpropionamidine).

In the *initiation* stage of this polymerization (Figure 3), thermal decomposition of the azo-initiator generates two free radicals, which subsequently add to the double bond of the MMA monomer. Once initiated, successive additions of MMA monomers to the free radical end of the polymer chain causes the chain to grow (*propagation* stage). In each step, the consumption of a

free radical is accompanied by the formation of a new, larger free radical. Eventually, in the *termination* stage, the polymerization stops by steps that consume, but do not form, free radicals, such as the combination of two free radicals.
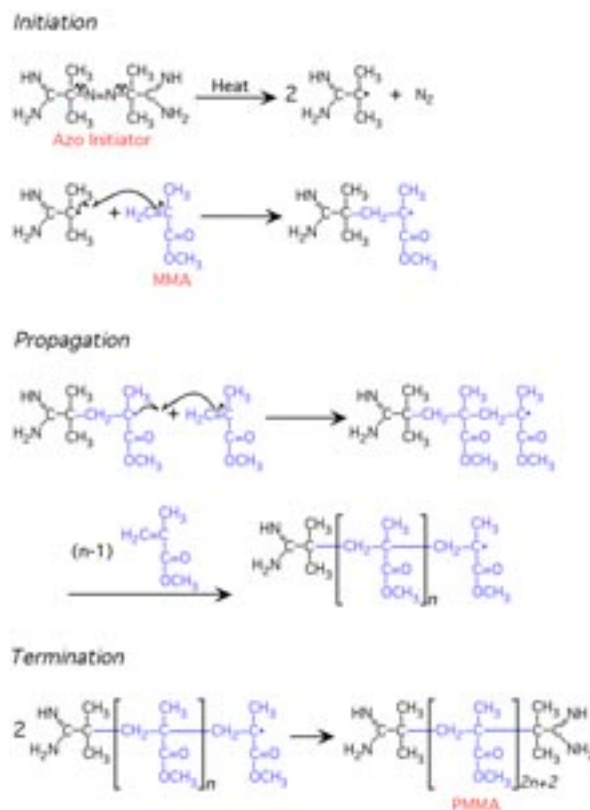
Figure 3. Free radical chain-growth polymerization of MMA using the azo-initiator 2,2'-azobis(2-methylpropionamidine) to produce PMMA. *Initiation*: The initiator decomposes upon heating to form free radicals, which attack the double bonds of MMA, forming larger free radicals. *Propagation*: Successive additions of MMA monomers increase the polymer size. *Termination*: Growth ceases when two radicals react. The initiator is incorporated into the polymer, forming amine end groups.

The product of the polymerization performed in this lab initially takes the form of a colloidal suspension of solid particles that are so small that they tend not to settle. With careful control of reaction conditions, the PMMA forms uniformly sized spherical particles.[1] By centrifuging, the PMMA particles can be forced to settle and pack into a solid, called a colloidal crystal. In this colloidal crystal, the PMMA spheres are arranged in a close-packed fashion in the same manner as the silica spheres that make up natural opals. These materials can, therefore, be referred to as *synthetic opals*. A scanning electron micrograph (SEM) of a PMMA colloidal crystal (synthetic opal) is illustrated in Figure 4.
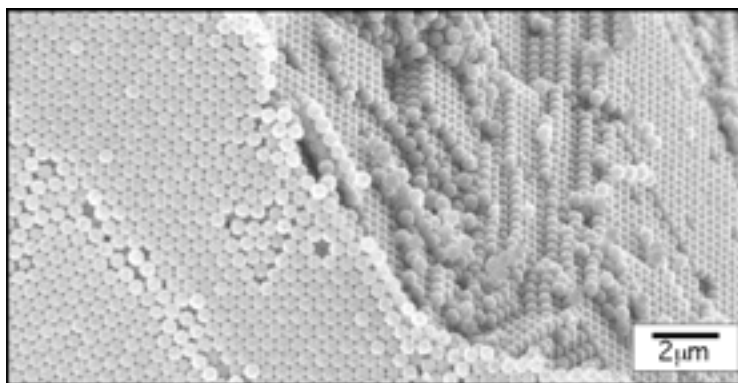
Figure 4. SEM of a PMMA colloidal crystal illustrating the close-packed layers of PMMA spheres. Spheres typically pack in a face-centered cubic structure, wherein each sphere contacts 12 others (6 in the same layer, 3 in the layer above, and 3 in the layer below).

C. Sol-gel chemistry

The second part of the lab exercise involves the formation of a solid structure around the PMMA colloidal crystals by the process of sol-gel chemistry.[2] In the system here, a *sol* is a solution of polymerizable metallo-organic species. A *gel* is a continuous solid network (a very large molecule) surrounding and supporting a continuous liquid phase. In the sol-gel process, network solids are formed by the reactions of hydrolysis and condensation. These reactions are illustrated in Figure 5 for tetramethoxysilane (TMOS), $Si(OCH_3)_4$, which is the chemical used in this lab exercise for the preparation of silica (SiO_2). In the hydrolysis step, TMOS reacts with water, resulting in the replacement of an alkoxy group (-OCH_3) by a hydroxyl group (-OH) and the liberation of methanol (CH_3OH). *Because methanol can be somewhat toxic, tetraethoxysilane, TEOS, is actually a preferred starting material (the product is ethanol).* Condensation reactions, which lead to growth of the network solid, occur between a hydroxyl group and an alkoxy group (alcoxolation), or two hydroxyl groups (oxolation), liberating methanol and water in the process. As this growth process continues, a sol of small chains or branched structures form. These chains continue to grow, and they eventually gel to form a continuous network solid, at which point the material changes from liquid to solid. The sol-gel process is complete upon removal of the solvent and the organic products generated from the sol-gel reaction.

$$(CH_3O)_3Si-OCH_3 + H_2O \xrightarrow{\text{Hydrolysis}} (CH_3O)_3Si-OH + CH_3OH$$

$$\equiv Si-OH + CH_3O-Si \equiv \xrightarrow[\text{(alcoxolation)}]{\text{Condensation}} \equiv Si-O-Si \equiv + CH_3OH$$

$$\equiv Si-OH + HO-Si \equiv \xrightarrow[\text{(oxolation)}]{\text{Condensation}} \equiv Si-O-Si \equiv + H_2O$$
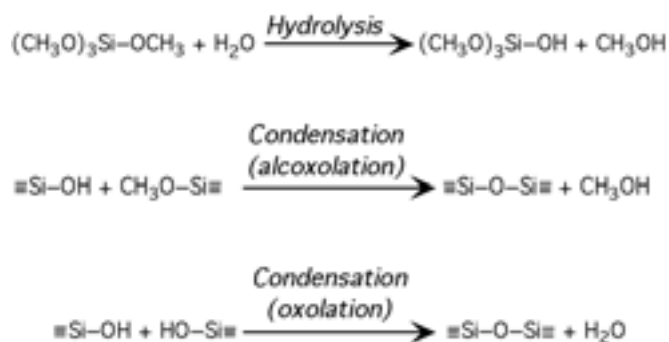
Figure 5. Hydrolysis and condensation of tetramethoxysilane to form silica. The three bars connected to the Si atoms in the condensation steps represent bonds to three other hydroxyl (-OH) or alkoxy (-OCH_3) groups.

D. Inverse opals

The second part of the lab exercise also involves the creation of inverse opals, which are inverse replicas of opals. Instead of consisting of a regular arrangement of uniform spherical particles (as in opals), inverse opals consist of a regular arrangement of spherical void spaces surrounded by solid walls. The inverse opals are made after solidification of the sol in the void spaces of the synthetic PMMA opals (as described above), by removing the PMMA template to leave a three-dimensionally ordered porous solid.[3,4] An SEM image of inverse opal silica is given in Figure 6.
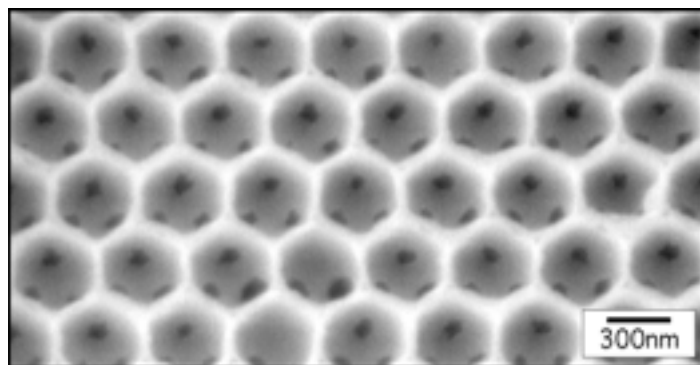
Figure 6. A scanning electron microscopy image of inverse opal silica illustrating a close-packed arrangement of pores. The white regions are walls around the top layer of pores, the gray regions are walls around the second layer of pores, and the black regions are windows connecting the pores.

In addition to the silica inverse opals made in this lab exercise, many other compositions of inverse opals can be made, including metal oxides, metals, semiconductors, and others.[5] The motivation for making inverse opals includes their use in catalysis, sorption, chromatography, battery materials, and as bioactive materials – uses that benefit from the highly accessible surfaces and relatively large pore sizes of these materials.[5] In addition, the ordered arrangement of the pore structure leads to diffraction of light in a manner similar to the diffraction observed with opals. These diffraction effects endow inverse opals with optical and photonic crystal properties that may be utilized for optical sensors and circuits, and to guide light waves.

The term "photonic crystal" is used to describe a material with a uniform repetition of low and high refractive index areas.[6,7] Inverse opals fit this definition, as they have a uniform arrangement of void spaces containing air (with a low refractive index of 1.000) and solid walls (with a higher refractive index, e.g. 1.455 for silica). A peculiar property of these materials is their ability to "filter" light. When white light, which contains all visible colors of light, is shined on a photonic crystal, some wavelengths are forbidden from passing through the material, being reflected instead (Figure 7). The remaining wavelengths are unaffected by the photonic crystal, and they simply pass through. For complete reflection, the refractive index of the wall material must exceed a value of 2.8. Significant reflection can be observed, however, even for lower values of the refractive index.
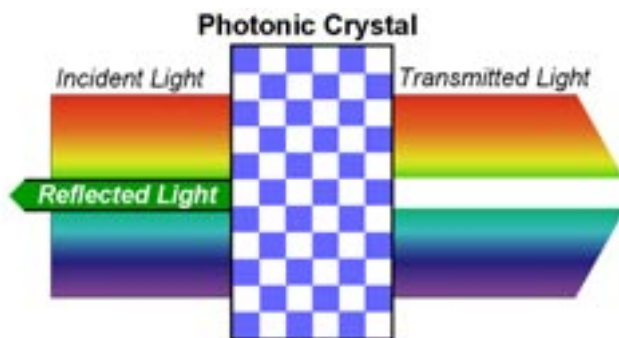
Figure 7. Interaction of white light (which contains all visible colors) with an inverse opal photonic crystal. When white light impinges upon a photonic crystal, a range of light wavelengths is reflected, while the remaining light is transmitted.

2. Equipment, chemicals, and setup

A. Equipment needed for emulsion polymerization
1. Round-bottom flask (5 neck, 3 L), with rubber or glass stopper
2. Funnel
3. Cylindrical heating mantle (3L)
4. Temperature controller (Barnant Company)
5. Thermocouple probe (Type K, 1/16"), used with an NMR tube, one-hole stopper, and parafilm
6. Support stand (36") with three-finger clamp and clamp holder (for condenser) and clamp holder (for stirrer)
7. Water-cooled condenser, with rubber tubing (three, about 4' each), small hose clamps (two), one-hole stopper, glass tubing (4"), glass pipette (disposable), Erlenmeyer flask (300 mL, for bubbler), and parafilm
8. Electric lab stirrer, with thick rubber hose (3" long, 10 mm i.d., 23 mm o.d.), hose clamps (two), and high-temperature tape
9. Glass stirring shaft (10 mm diameter, 58 cm long)
10. Teflon stirrer blade for glass stirring shaft (1.9 cm wide, 7.6 cm long)
11. Bearing and adapter set for glass stirring shaft
12. Nitrogen gas cylinder (or house N_2 gas), with rubber tubing (3'), one-hole stopper, and glass pipette (disposable)
13. Graduated cylinders (100 and 500 mL)
14. Electric balance and weighing paper
15. Metal spatula
16. Screw driver (for hose clamps)
17. Insulated gloves (for handling the hot reaction flask)
18. Cork ring (stand for cooling round-bottom flask)
19. Glass wool
20. Plastic container (4 L) with cover
21. Centrifuge (Fisher Marathon Model 8K)
22. Bucket rotor for centrifuge
23. Round centrifuge buckets (four)
24. Round-bottom glass centrifuge tubes (four, 100 mL each) and Parafilm

25. Small beakers (to hold the tubes upright during PMMA drying)
26. Glass slides – optional (for testing the opalescence of the PMMA)
27. Ordering information for the specialized items listed above can be found in the Appendix. These items, including the heating and stirring apparatuses, are the recommended (*i.e.*, best practices) equipment for this procedure. Due to the sensitivity of PMMA sphere size to the polymerization reaction conditions, it is necessary to have strict control of the heating and stirring to produce uniform polymer spheres. If the temperature is carefully regulated, however, a simple oil or water bath, and a thermometer inserted through a one-hole stopper into the reaction flask, may be used instead of the cylindrical heating mantle, temperature controller, and thermocouple probe. Any electric lab stirrer (with speeds of 300-400 rpm) with a shaft and stirrer blade may be used, but the bearing and adapter set are necessary to maintain a sealed system. Any model centrifuge (with rotor, buckets, and tubes) with speeds of 1000-2000 rpm can be used.

B. Preliminary equipment setup for emulsion polymerization

The apparatus for the preparation of monodisperse PMMA spheres by emulsion polymerization is illustrated in Figure 8. Due to the complexity and time-consuming nature of this setup, instructor assembly of the polymerization apparatus prior to the lab period is highly recommended. Some of the following steps may not apply to research labs where pre-existing equipment is in place, so the instructions may be adapted to fit the individual laboratory and available equipment.

1. In a ventilated hood, set the cylindrical heating mantle on the base of a support stand. Place the temperature controller beside the heating mantle, then plug the mantle and the thermocouple into the back of the temperature controller. Carefully insert an NMR tube into a one-hole stopper with the open end on top. **Caution:** *Never push a glass tube by the end. Instead, hold it near the stopper opening, and insert by wetting with a small amount of water and slowly turning the tube.* Holding the NMR tube in the rubber stopper upright, fill it with water, then thread the thermocouple wire into the tube until it touches the bottom. Seal the NMR tube shut with Parafilm. This arrangement allows the temperature of the emulsion polymerization reaction to be monitored in the round-bottom flask by the thermocouple wire while maintaining a sealed system with the stopper.

2. Attach a water-cooled condenser to the support stand using a three-finger clamp and a clamp holder. Fasten two rubber tubes (of appropriate length to reach a faucet and drain) to the condenser using hose clamps. Attach the free end of the bottom tube to the cold-water faucet and place the free end of the top tube into the drain. Insert a glass tube about 4 inches in length carefully into a one-hole stopper. Place this stopper into the top of the condenser. Attach one end of a third rubber tube to the end of the glass tube. Insert a disposable glass pipette into the opposite end of this tube, and place the pipette into a 300 mL Erlenmeyer flask filled with water. Wrap the top of the flask loosely with Parafilm to hold the tube and pipette in place. This bubbler arrangement will prevent a back-flow of room air into the flask during the reaction, assuring the system will be under a positive pressure of Nitrogen gas.

3. Insert a disposable glass pipette into a one-hole stopper. Attach one end of a rubber hose to the pipette and the other end to a nitrogen line. Ensure that the glass pipette is sufficiently long to be submerged during the emulsion polymerization procedure to allow nitrogen to bubble into the liquid. This prevents the formation of oxygen free radicals, which would inhibit polymer growth.

4. Mount the electric lab stirrer onto the support stand using a clamp holder. Wrap a few rounds of high-temperature tape around the metal stirrer shaft. Cut out a 3-inch length of thick rubber hose (10 mm inner diameter, 23 mm outer diameter). Attach the hose to the metal stirrer shaft and secure it with a hose clamp. Place another hose clamp on the other end of the hose for later attachment of the glass stirring shaft.

5. Using Figure 9 as a guide, assemble the bearing and adapter set. Insert the Teflon inner bearing into the threaded glass adapter, followed by the compression saddle and o-ring. Screw the bushing into the glass adapter until snug, then tighten the lock nut. Place the Teflon stirrer blade on the glass stirring shaft. Slip the bearing and adapter set over the glass stirring shaft. Insert the stirring apparatus into the central neck of the round-bottom flask. Make sure that the stir blade remains upright. It may be necessary to insert a spatula or wire into another neck of the flask to flip the blade upright. Keep the stir blade about one inch from the bottom (close enough to the bottom so that the stir blade cannot flip over). Lower the electric stirrer and insert the top of the glass stirring shaft into the hose affixed to the electric stirrer. Secure the shaft to the hose by tightening the hose clamp.
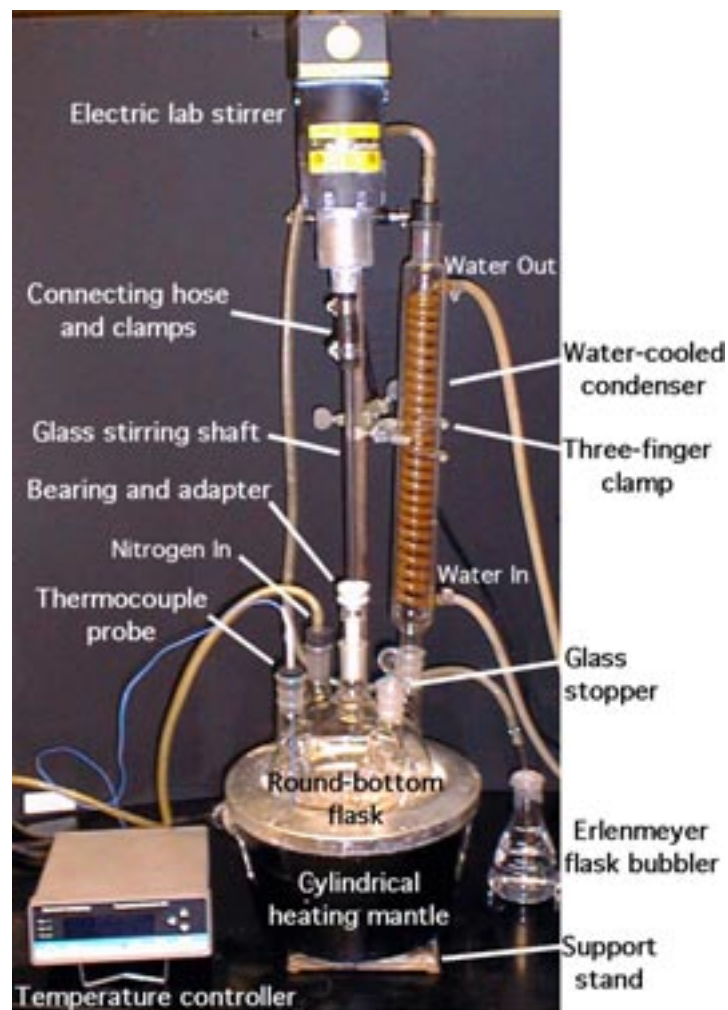
Figure 8. Emulsion polymerization apparatus. The stirring assembly is inserted in the central neck of the 5-neck round-bottom flask. Three other necks are used to attach a nitrogen line, thermocouple probe, and water-cooled condenser. The remaining neck is used for the addition of reagents, and is covered by a stopper during the reaction.

Figure 9. Left: Assembly of the bearing and adapter set. Right: Assembly of the stirring apparatus.

C. Chemicals needed for emulsion polymerization
1. Methyl methacrylate (MMA), (300-400 mL)
2. 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (1.5 g)
3. Distilled, deionized water (1600 mL)
4. Tetrahydrofuran (THF), (for cleanup)
5. Acetone, (for cleanup)

Ordering information for the chemicals can be found in the Appendix. Use care in the handling of all chemicals and observe safe lab practices. Wear goggles, gloves, and a lab coat. Perform all experiments in a ventilated hood. MMA has a strong odor and may be harmful by inhalation or skin absorption; avoid prolonged or repeated exposure and don't breathe the vapor. MMA is a flammable liquid; keep away from all sources of ignition. THF and acetone are harmful and extremely flammable liquids; prevent contact and keep away from ignition sources.

D. Equipment needed for sol-gel templating
1. Electric stir plate
2. Small glass vials (20 mL)
3. Magnetic stir bar (3/8")
4. Filtering flask, used with rubber tubing and vacuum line
5. Neoprene adapter
6. Büchner funnel with filter paper
7. Drying dish (small plastic dish to hold the samples while drying)
8. Disposable glass pipettes with bulbs
9. Metal spatula

10. Graduated cylinder (10 mL)
11. Programmable muffle furnace, equipped with an injection port kit (a
    standard furnace can be used with manual operation; see text)
12. Porcelain crucibles
13. Glass microscope slides (to observe the opalescence of the samples)
14. Microscope – optional (to observe the opalescence of the samples)

The equipment listed above are the preferred items for this procedure, however, not all of them are required. The electric stir plate and magnetic stir bar are used to mix the sol-gel reagents prior to templating. Alternatively, adding the reagents one at a time to a vial and drawing the fluid in and out of a glass pipette will mix the reagents adequately. This procedure generally works better than stirring with a glass rod. A programmable muffle furnace is preferred for reasons of safety and product quality. Controlled heating ramps prevent ignition and rapid burning of the samples, avoiding a potential fire hazard. In addition, slow heating ramps allow the inverse opal walls to uniformly condense while the PMMA slowly burns away, producing well-ordered samples. If a programmable furnace is not available, a standard furnace can be used, *but only for the silica inverse opals.* In this case, the temperature should be raised manually in 50° increments, with 30 minutes spent at each intermediate temperature (the 10 hour hold at $600\,^{\circ}\text{C}$ is still required). Büchner funnels are recommended over glass-frit funnels, which will become clogged and difficult to clean in this procedure. Ordering information for the specialized items listed above can be found in the Appendix.

E. Chemicals needed for sol-gel templating
1. PMMA spheres (prepared in the first part of this lab), (10 g)
2. Tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS), (6 mL)
3. Methanol or ethanol (4 mL)
4. Distilled, deionized water (3 mL)
5. Concentrated hydrochloric acid (HCl), (1 mL)

Ordering information for the chemicals can be found in the Appendix. Use care in the handling of all chemicals and observe safe lab practices. Wear goggles, gloves, and a lab coat. Perform all experiments in a ventilated hood. TMOS and methanol are interchangeable with TEOS and ethanol, but for reasons of safety (lower toxicity) the TEOS/ethanol combination is preferred. TMOS and TEOS are harmful if swallowed, inhaled, or absorbed through skin, and are highly flammable. Do not breathe the vapor, prevent contact with skin and eyes, and avoid sources of ignition. Methanol and ethanol are harmful and extremely flammable. Prevent contact with skin and eyes, do not breathe the vapor, and avoid all sources of ignition. Hydrochloric acid (HCl) can cause severe burns, and its vapor is extremely irritating; prevent contact with skin and eyes, do not inhale, and always use in a hood.

3. Making the polymer sphere templates

A. Experiment overview
Before inverse opals can be synthesized, it is necessary to prepare the PMMA sphere colloidal crystal templates. Due to the complexity of the emulsion polymerization apparatus, it is recommended that the polymer spheres be produced in large batches by the instructor or by

teams of students. The size of the polymer spheres directly affects the pore size of the inverse opals, which in turn affects the color of light reflected by the inverse opals. It is recommended that each group prepares a different size batch of spheres (if multiple batches are prepared) or the instructor prepares different sizes of PMMA spheres prior to the lab period. This will allow for comparisons of the optical properties of the products to be made.

The entire process - from the synthesis of a colloidal suspension of PMMA through the attainment of ready-to-use PMMA template spheres - takes roughly one week (Figure 10). We recommend assembly of the complex components of the polymer apparatus by the instructor prior to the laboratory period (detailed in Figure 8 and the discussion above). The emulsion polymerization procedure requires the heating of a large quantity of water and methyl methacrylate (MMA) to 70 or 80 °C, which may require up to two hours. The instructor may choose to begin heating the mixture before the lab period begins to save time. Follow-up centrifuging and water decanting is also required. It is left up to the instructor's discretion whether to handle these follow-up procedures, or to designate students to carryout these steps.

Table 1 provides a good guideline to follow in the preparation of PMMA spheres. Templating with these three sphere sizes will produce inverse opals with distinctly different reflected colors. The parameters may be adjusted to produce PMMA spheres of intermediate sizes. To make larger spheres, use more MMA (while keeping the amount of water constant), use a lower temperature, or use less initiator. To make smaller spheres, use less MMA, use a higher temperature, or use more initiator. We recommend following the recipes in Table 1 as these PMMA sizes will produce inverse opals with light reflections in the visible region. Spheres of smaller or larger sizes will lead to products without visible reflections.

Using the parameters in Table 1 will lead to inverse opal silica materials that appear blue-violet, green, and orange-pink in reflected light for the small, medium, and large PMMA-templated products, respectively. Each preparation will yield in excess of 250 grams of PMMA. Quantities may be scaled-down as appropriate to fit the class size. Use care in the handling of all chemicals and observe safe lab practices. Wear goggles, gloves, and a lab coat during this experiment. Perform all experiments in a ventilated hood.
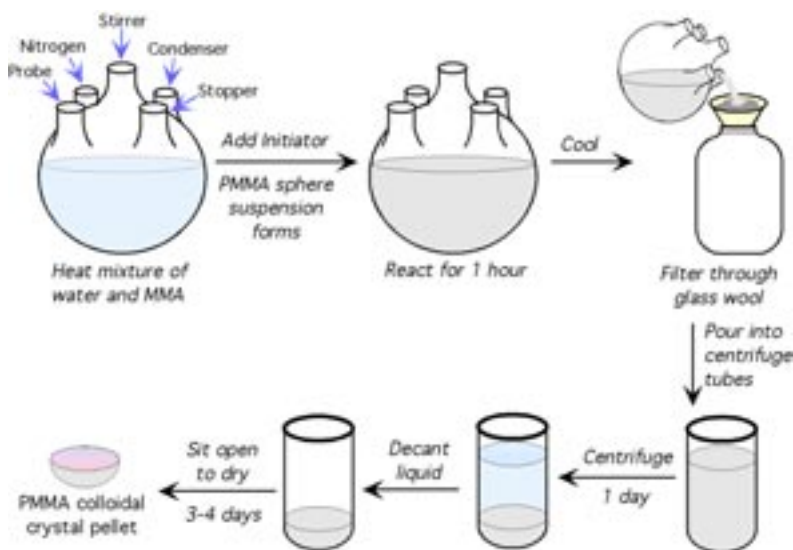
Figure 10. Schematic of the preparation of PMMA spheres by emulsion polymerization and the formation of colloidal crystals by centrifuging. A sign of a successful polymerization is bright opalescence of the PMMA colloidal crystal pellet.

Table 1. Recommended parameters for the preparation of PMMA spheres. The *small*, *medium*, and *large* designations refer to the PMMA sphere diameters, and to the pore sizes of the inverse opals produced by these spheres. These are arbitrary designations, made only for comparison purposes and ease of discussion.

Sample	Approximate diameter	Water volume	MMA volume	Temp.	Initiator mass
Small	310 nm	1.6 L	300 mL	80 °C	1.5 g
Medium	375 nm	1.6 L	300 mL	70 °C	1.5 g
Large	425 nm	1.6 L	400 mL	70 °C	1.5 g

B. Emulsion polymerization procedure
1. Using Figure 8 as a guide, place the 5-neck round-bottom flask into the cylindrical heating mantle and insert the stirrer assembly, nitrogen line, water-cooled condenser, and thermocouple probe into the necks of the flask. Make sure that the stirrer blade is upright.

2. Insert a funnel into the open neck of the flask for the addition of reagents. Using a graduated cylinder, measure out 1.6 L of distilled, deionized water and pour it into the reaction flask. Select your choice of PMMA size from Table 1 and add the appropriate quantity of MMA to the flask. Remove the funnel and insert a rubber or glass stopper into this neck.

3. Turn on the nitrogen gas. The flow rate should be very slow (approximately 3-4 bubbles per second). The slow flow rate is necessary to prevent pressure build-up in the reaction flask.

4. Turn on the water for the condenser. Again, only a very slow flow of water is needed.

5. Turn on the electric stirrer to a speed of approximately 350 rpm, (this corresponds to a stir setting of about 2.5 for the model of stirrer listed in the Appendix).

6. Using the arrows on the Temperature Controller, set the temperature to 70 or 80 ºC (following Table 1 parameters for your choice of PMMA size), and press "Tune" (an indicator light will turn on). The reaction mixture will heat-up and stabilize at the chosen temperature, at which time the indicator light will turn off. The temperature of the reaction mixture will appear on the screen of the Temperature Controller throughout the heating process. This process may require two hours if cold water was used in the synthesis. It is very important to the quality of the PMMA spheres produced for the temperature to have stabilized before continuing to the next step.

7. When the temperature has stabilized at the desired level (70 or 80 ^{o}C), turn off the nitrogen gas. Leave the nitrogen line and one-hole stopper in the flask.

8. Place a piece of weighing paper on a balance, zero it, and weigh out 1.50 g of 2,2'-Azobis(2-methylpropionamidine) dihydrochloride initiator. Remove the stopper from the reaction flask, add the initiator, and replace the stopper. Within a few minutes, a white milky colloidal suspension will form. The synthesis will be complete within 1 to 1.5 hours. The temperature of the reaction mixture typically rises 5 to 10 ºC over this period, and then decreases to the original temperature. This is perfectly normal and indicates the reaction is in progress. No manual adjustment of the temperature is needed, just leave the apparatus untouched.

9. Turn off the Temperature Controller after 1 hour if the temperature has stabilized at its initial value. If the temperature hasn't stabilized after 1 hour, wait another 30 minutes before turning it off. Remove the thermocouple probe and nitrogen line from the flask.

10. Turn off the Electric Stirrer. Raise the stirrer a few inches by adjusting the clamp holder up the support stand. Loosen the hose clamp on the rubber hose that attaches the glass stir shaft to the Electric Stirrer, and carefully pull the glass stir shaft down to detach it from the stirrer.

11. Turn off the water and raise the condenser out of the flask by loosening the three-finger clamp, lifting the condenser, then tightening the clamp.

12. Wearing insulated gloves, very carefully lift the flask out of the cylindrical heating mantle and onto a cork ring (we recommend that the instructor handle hot reaction flasks). Allow the sample to cool for at least one hour.

13. Insert a funnel into a large (4 L) plastic container. Place glass wool in the funnel. Slowly pour the PMMA suspension through the glass wool in the funnel (this will remove any large chunks of PMMA). A benchmark for a successful synthesis is opalescence of the sample. A good way to view this is to dip a spatula into the liquid and smear a little on a dark bench top. As it dries, a good sample will look colorful (Figure 11). You can also try dipping a glass slide into the liquid, then pulling it out. After it dries it will be opalescent, appearing different colors depending upon the angle of observation.
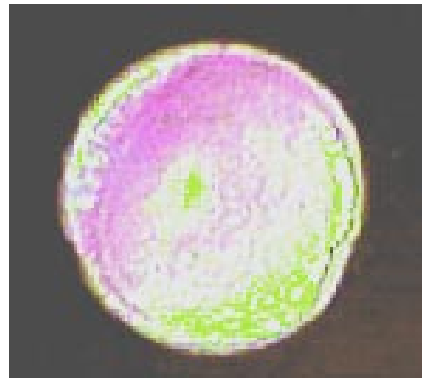
Figure 11. Left: Photograph of a PMMA colloidal suspension smeared on a black bench top. A successful preparation will yield a sample that changes from a white milky liquid to a colorful iridescent powder upon drying. Right: Photograph of a dried PMMA colloidal suspension on a glass slide. A successful product will appear colored, and change colors with angle of observation.

C. Cleanup of polymerization apparatus

Clean the flask and stirring apparatus with water. If any PMMA remains stuck to the flask or stirrer (which is usually the case), the instructor should add a 50:50 mixture of THF and acetone to the flask, and heat at 50 ºC for a few hours. This solvent mixture will dissolve any remaining polymer. Pour the solvents into a waste bottle when done, and rinse the flask and stirrer with acetone.

D. Packing the spheres into a colloidal crystal

1. Place the centrifuge tubes into their buckets, and fill the tubes with the colloidal PMMA suspension. Add the same amount to each tube to ensure the centrifuge will be balanced (placing samples with different weights into a centrifuge will cause it to shake vigorously). Cover the tubes with Parafilm. Place the buckets on the rotor in the centrifuge. Close the cover and set the rotation rate at about 1500 rpm. Start the centrifuge, and let the samples spin for one day.

2. Stop the centrifuge, and remove the samples. You should see a clear liquid in the top portion of tubes, and a white solid at the bottom. If you don't see this separation, the samples will require further centrifuging. Carefully decant (pour gently) the liquid into a waste bottle. Set the centrifuge tubes containing the PMMA colloidal suspensions upright in small beakers. Let the samples sit open for 3 to 4 days to dry. The samples are dry when the colloidal crystal pellets of PMMA easily come out of the tubes when tipped over. High quality PMMA will exhibit bright opalescence on the top surface of the pellet (Figure 12).


Figure 12. Photograph of the smooth top surface of a PMMA colloidal crystal pellet illuminated with white light. A benchmark of a successful polymerization is the appearance of opalescence with intense colors.

4. Making the inverse opals by sol-gel templating

A. Experiment overview

In this portion of the lab exercise, the PMMA colloidal crystals prepared in the previous step are used to template the formation of inverse opals. This preparation involves the vacuum infiltration of PMMA spheres by a sol-gel precursor and removal of the template by calcination (which is heating to burn away the polymer, see Figure 13). The samples can be placed in the furnace, and the calcination process can be started during the lab period. The entire calcination requires roughly one day, so follow-up removal of the samples will be required (safety reminder: do not remove samples from the oven until they have cooled completely). Depending upon the number of samples and size of the furnace, some samples may have to be calcined on following days. It is left to the instructor's discretion whether to handle these follow-up procedures, or to designate students to carryout this work. Use care in the handling of all chemicals and observe safe lab practices. Wear goggles, gloves, and a lab coat during this experiment. Perform all experiments in a ventilated hood.
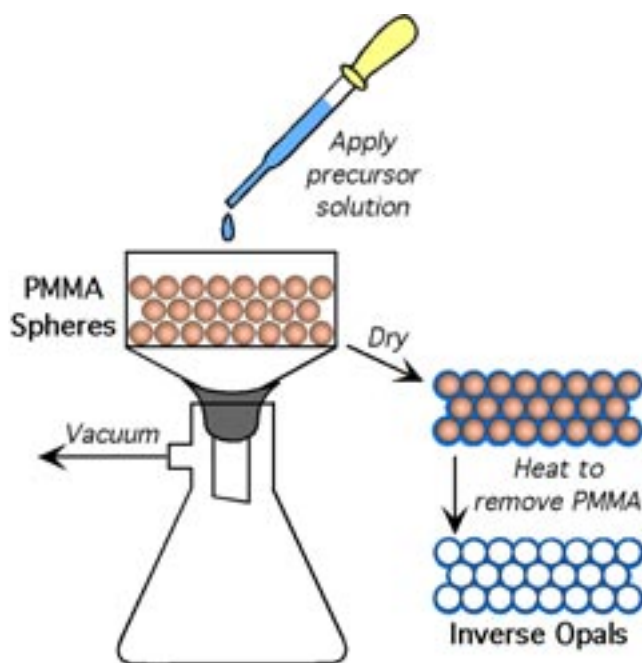
Figure 13. Schematic of the preparation of inverse opals by sol-gel templating (the sizes of the PMMA spheres are greatly exaggerated for illustration purposes). PMMA colloidal crystal templates are placed in a Büchner funnel, and then infiltrated with sol-gel precursors, dried, and heated at high temperatures to remove the PMMA and cure the walls of the inverse opal product.

B. Sol-gel templating procedure

1. Using Figure 13 as a guide, place a neoprene adapter in the neck of a filtering flask, and then insert a Büchner funnel. The adapter is used to create a sealed system when a vacuum is applied, so that liquids added to the Büchner funnel will be forced into the filtering flask. Connect one end of a rubber tube to the filter flask, and the other end to a vacuum line.

2. Place a piece of weighing paper on a balance, zero it, and weigh out about 10 g of dry PMMA (roughly one pellet of PMMA). Place the PMMA pellet onto a paper towel, and using a metal spatula lightly crush the PMMA into a powder. Set this PMMA powder aside for later use.

3. In a well-ventilated fume hood, place a small glass vial (20 mL) on an electric stir plate, and insert a magnetic stir bar. Turn on the stir plate so that the stir bar slowly rotates (if this shakes the vial, secure it in place with a three-finger clamp). Using a small graduated cylinder, measure out 4 mL of methanol (or preferably, ethanol). Add the methanol (or preferably, ethanol) to the glass reaction vial using a pipette. Measure out 6 mL of TMOS (or preferably, TEOS), using a pipette to transfer the liquid from the bottle to the graduated cylinder. Add the TMOS (or preferably, TEOS) to the glass vial using a pipette. The liquids will mix (if they aren't mixing, turn up the stir rate a little). Now measure out 3 mL of distilled, deionized water and add it to the glass vial in the same manner as above. Next, carefully measure out 1 mL of concentrated hydrochloric acid (HCl), using a pipette to transfer the HCl from the bottle to the graduated cylinder. (Caution: never try to pour concentrated acids from a bottle, they are extremely corrosive and will cause severe burns if they come in contact with skin or eyes. If HCl comes in contact with skin or eyes, immediately wash with large amounts of water.) Using a pipette, add the HCl dropwise to the reaction vial. Be careful, rapid addition of HCl will cause the mixture to boil.

4. Turn on the vacuum line to a very low setting. Place a piece of filter paper in the Büchner funnel. Using a pipette, completely wet the filter paper with methanol (or preferably, ethanol). The filter paper should seal to the funnel. If the filter paper does not adhere, apply more methanol (or preferably, ethanol) and flatten the filter paper with a spatula. Pour the PMMA powder onto the filter paper in the Büchner funnel. Using a metal spatula, spread and lightly pack the PMMA so it evenly covers the entire filter paper (the powder should be less than a half centimeter thick; if a small Büchner funnel is used, you should use less PMMA).

5. Turn the vacuum line on its highest setting (a low vacuum setting can lead to dense solids rather than porous ones). Using a pipette, carefully drip about 10 mL of the sol-gel solution prepared above (in step 3) over the entire surface of the PMMA, being careful to wet all of the PMMA before running out of liquid. This can be a bit tricky. Slowly drip the liquid on the PMMA back-and-forth across the upper surface of the PMMA powder so that the entire surface is wetted uniformly. Only use leftover sol-gel liquid if the liquid coverage is not uniform, as the addition of too much liquid can lead to dense solids instead of porous solids. If not all of the PMMA is coated, it is not necessary to prepare any more sol-gel solution; the yield will simply be a bit smaller. Let the vacuum line continue to run on high for about 20 minutes (this will speed the drying of the sample).

6. Turn off the vacuum. Using a spatula to loosen the filter paper from the Büchner funnel, remove the filter paper containing the sample and scrape the powder into a small drying dish. Let the sample sit open to dry for at least 30 minutes. Drying time is less critical for the inverse opal silica prepared in this lab experiment than it is for some other inverse opal compositions. Rinse the Büchner funnel, filter flask, and glass reaction vial with methanol (or preferably, ethanol), pouring all waste into a waste bottle. Wash all equipment with soap and water.

C. Removing the polymer sphere template

1. Pour the dry PMMA/silica powder (obtained in the previous section) into a porcelain crucible, and insert the crucible into a programmable muffle furnace equipped with an injection port for the introduction of air. Multiple samples can be put in the furnace at the same time, just be sure to write down the arrangement of samples on a piece of paper so they don't get mixed up.

2. Turn on the air supply to the furnace to a low level. Set the temperature program as follows:

    (a) Ramp the temperature at 2 °C/minute from room temperature to 300 °C
    (b) Hold at 300 ºC for 2 hours
    (c) Ramp the temperature at 2 °C/minute from 300 ºC to 550 °C
    (d) Hold at 550 ºC for 10 hours
    (e) Ramp the temperature at 10 °C/minute from 550 ºC to room temperature

3. After the furnace has cooled to room temperature, remove the crucibles, and pour each sample into a different glass vial. High quality samples will immediately be apparent by their opalescence and relatively intense reflected colors. Stopper the vials and label the samples. Turn off the furnace and the air supply after all the calcinations are complete.

5. Optical properties of inverse opals

A. Viewing the colors of inverse opals

The benchmark of a successful synthesis of inverse opal silica photonic crystals is the appearance of opalescence and brightly reflected colors. A good way to make these photonic crystal properties more apparent is to spread a thin layer of the sample on a glass microscope slide, place another slide directly on top of this, then tape the slides together at the ends. For best viewing of the reflected color, place the slides on a dark surface. High quality inverse opal samples will appear brightly colored (Figure 14). The three inverse opal silica samples prepared in this laboratory guide (with small, medium, and large pores) will appear blue-violet, green, and orange-pink, respectively. You will notice that as the pore size of the inverse opal increases, the wavelength of light reflected by that sample also increases.
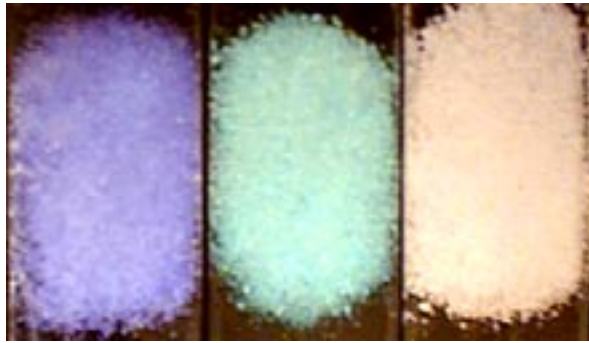
Figure 14. Photograph of the three sizes of inverse opal silica powder held between glass microscope slides, observed in reflected light. The small, medium and large pore inverse opal silica samples appear blue-violet, green, and orange-pink, respectively, due to diffraction of light of successively longer wavelengths.

Small   Medium   Large

It is important to note that the color of photonic crystals depends entirely on diffraction, and is independent of electronic processes. Most other colorful materials derive their color by the absorption of visible light, which causes electronic transitions that give off colors. When a substance absorbs certain wavelengths of visible light, its color is determined by the wavelengths of visible light that remain. The substance exhibits the color that it reflects, which is complementary to the color of light that it absorbs. Silica appears white because it does not absorb any light wavelengths in the visible region. Silica inverse opals, on the other hand, appear colored – not due to absorption of light, but instead due to diffraction of light from the periodic arrangement of the uniformly sized pores. An important consequence of this difference in the origin of color is our ability to observe two components of the light instead of one. As with other colored substances, we can see the light that an inverse opal reflects. But, unlike other colored substances, the inverse opal does not absorb the complementary color; this color is instead transmitted through the inverse opal (Figure 15).

These optical properties can easily be observed in your inverse opal material by holding the sample against a dark surface to see the reflected color, and holding it up to the light to see the complementary transmitted color. The colors may not be very prominent if the lab room has very bright lights, so try dimming the lights and using a flashlight as a light source if you have difficulty seeing these optical effects. Figure 16 illustrates photographs of how the medium pore inverse opal silica sample should appear in orientations with the observer and light source on the same side and on opposite sides of the inverse opal. You'll notice that the sample looks green when light is reflected from its surface, and pink when light is transmitted through it.
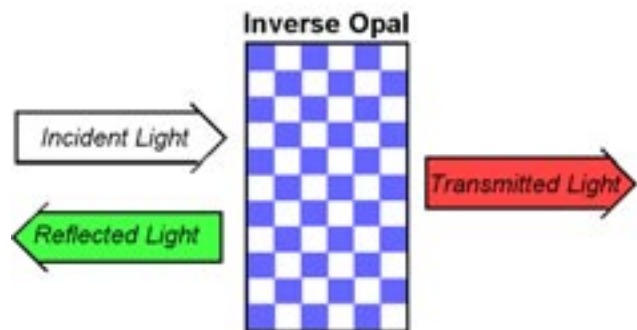
Figure 15. Observed behavior of the interaction of white light (which contains all visible wavelengths) with inverse opal photonic crystals. When white light strikes the sample, it is separated into two components: light of one color is reflected from the surface of the inverse opal, while light of the complementary color is transmitted through the inverse opal.

Samples with different pore sizes will exhibit a similar complementary relationship between the transmitted and reflected colors. If your lab has a microscope, put a small amount of inverse

opal silica powder on a glass slide and observe it under magnification. The opalescence observed through a microscope is much greater than that observed without a microscope.
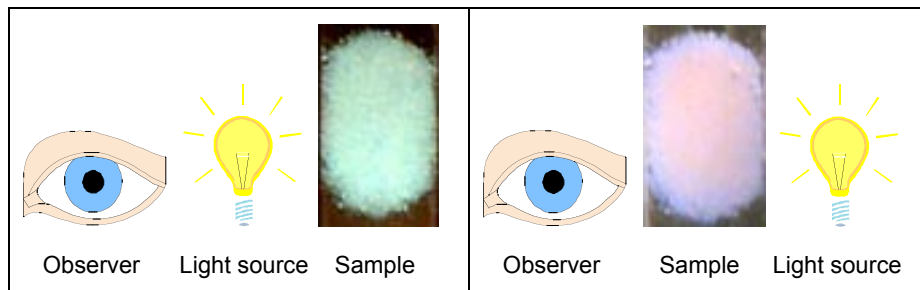
Figure 16. Left: Photograph of an inverse opal silica powder (with medium sized pores) with the observer and light source on the same side of the sample – illustrating the color of reflected light. Right: Photograph of the same sample with the observer and light source on opposite sides of the sample – illustrating the color of transmitted light.

B. Predicting and changing the colors of inverse opals

As mentioned in the previous section, the wavelength of light reflected by an inverse opal is affected by the size of its pores. Pore size, however, is only one of several factors that influence the color of light reflected by an inverse opal. In addition, the solid fraction of the inverse opal (*i.e.*, the volume percent of the inverse opal that is occupied by solid walls), the refractive indices of the walls, and the void spaces affect this color. We can estimate the wavelength of maximum reflection (λ_{max}) by the equation[8,9]:

$$\lambda_{max} = 1.633\,D\,[\phi\,n_{walls} + (1-\phi)\,n_{voids}]$$

where D is the average pore size, ϕ is the solid fraction, and n_{walls} and n_{voids} are the refractive indices of the walls and void spaces, respectively.

You will notice that the wavelength of maximum reflection is directly proportional to the average pore size of the inverse opal. Even more interesting is the effect of the refractive index of the voids on the color of light reflected. The significance of this effect is that we can change the color simply by filling the pores with a solvent! You can try this by adding a few drops of methanol to a small amount of inverse opal powder in a glass vial, or by dripping some methanol along the edge of the glass slides containing your sample (Figure 17).
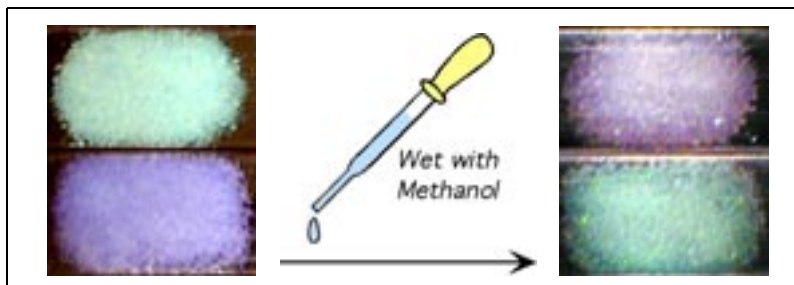
Figure 17. Left: Photograph of the small (bottom) and medium (top) inverse opal silica samples in reflected white light. Right: Photograph of the same samples (in reflected white light) after the addition of methanol. The colors of the samples change because of changes in the refractive index of the voids. The large pore sample turns white because the color shifts out of the visible region.

For the inverse opal silica samples prepared in this lab exercise, the value of the solid fraction is approximately 0.06, which means the solid walls occupy about six percent of the total volume of the inverse opal. Using this value, along with the refractive indices of silica ($n = 1.455$), air ($n = 1.000$), and methanol ($n = 1.329$), we can calculate the expected wavelengths of light reflected by the samples (Table 2).

Table 2. Typical inverse opal silica pore sizes obtained following the procedures detailed in this lab manual, and the expected wavelengths of maximum reflection for the air- and methanol-filled inverse opal silica samples. (Note: the pore size in inverse opals is typically 15% smaller than the diameter of the PMMA sphere templates due to shrinkage of the structure as the walls condense.)

Sample	SiO_2 pore size	λ_{max} (air)	λ_{max} (methanol)
Small	265 nm	445 nm	578 nm
Medium	320 nm	537 nm	698 nm
Large	360 nm	604 nm	786 nm

Extended work

If your lab is equipped with a Diffuse-Reflectance UV-VIS spectrometer, you can obtain spectra of the dry and solvent-filled samples. Since the pore size, the solid fraction, and the refractive index of the walls are all constant for a given inverse opal, the wavelength of light reflected varies linearly with the refractive index of the solvent filling its voids. A plot of the reflectance maxima versus the solvent refractive index should give a straight line. Recommended solvents for these measurements include: methanol ($n = 1.329$), ethanol ($n = 1.360$), isopropanol ($n = 1.377$), THF ($n = 1.407$), DMF ($n = 1.431$), toluene ($n = 1.496$), and dibromoethane ($n = 1.538$).

6. Additional compositions of inverse opals

In addition to inverse opal silica, numerous other inverse opal metal oxides can be prepared by making slight modifications to the sol-gel templating and template removal conditions described in the sections above.[3,4,10] Some possibilities include titania, alumina, and zirconia. To make inverse opals of these compositions, simply replace TMOS, methanol, water, and HCl in the procedure above by the appropriate metal alkoxide or metal acetate diluted in alcohol. Metal acetates are preferred, because the metal alkoxides are very reactive and water-sensitive, making them difficult to work with. One particularly interesting example is zirconia, which forms inverse opals with very intense colors when carefully prepared (Figure 18). These samples are opaque, however, so they don't change colors when held up to a light. Template removal conditions are often more stringent with compositions other than silica. Unlike silica, which has amorphous walls, most other materials have walls composed of small crystal grains. If heated too long or at too high a temperature, these crystals grow and eventually become larger than the pores, resulting in the destruction of the uniform pore structure.
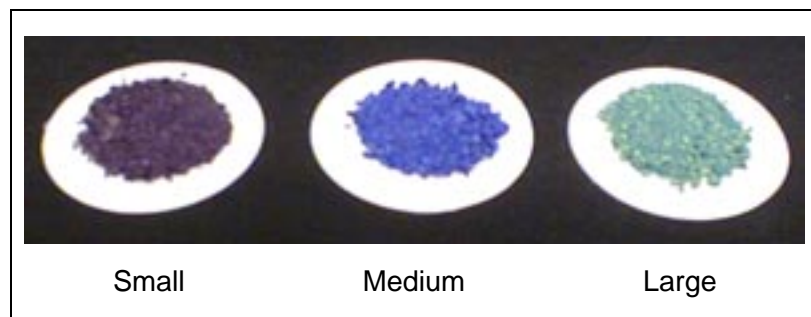
Small   Medium   Large

Figure 18. Photographs of inverse opal zirconia prepared from small, medium, and large PMMA and a 50:50 solution of zirconium acetate solution in dilute acetic acid mixed with methanol. The template was removed from these samples by heating under a mixture of air and nitrogen by slow ramping to 450 °C, then holding for 2 hours. The samples appear violet, blue, and green due to the diffraction of successively longer wavelengths of light.

7. Appendix

A. Ordering and vendor contact information for emulsion polymerization equipment

Item	Ordering Code	Vendor	Price ($)
Round-bottom flask	CG-1535-04	ChemGlass	184
Cylindrical heating mantle	11-474-36	Fisher Scientific	209
Temperature controller	15-176-110	Fisher Scientific	770
Thermocouple probe	15-077-45	Fisher Scientific	24
Support stand	14-670D	Fisher Scientific	46
Water-cooled condenser	CG-1215-A-10	ChemGlass	173
Electric lab stirrer	14-499-10	Fisher Scientific	520
Glass stirring shaft	8075-14	Ace Glass	36
Teflon stirrer blade	8085-11	Ace Glass	8
Bearing and adapter set	8066-43	Ace Glass	69
Centrifuge	04-977-8K	Fisher Scientific	2549
Bucket rotor	04-976-5100	Fisher Scientific	809
Round centrifuge buckets	04-976-200RWC	Fisher Scientific	Two for $390
Centrifuge tubes	04-974-100AT	Fisher Scientific	Two for $88
Centrifuge plastic adapter	04-974-200A	Fisher Scientific	Four for $164

Ace Glass P.O. Box 688 1430 Northwest Blvd. Vineland, NJ 08362 1-800-223-4524 www.aceglass.com	ChemGlass 3861 North Mill Rd. Vineland, NJ 08360 1-800-843-1794 www.chemglass.com	Fisher Scientific 4500 Turnberry Drive Hanover Park, IL 60103 1-800-766-7000 www.fishersci.com

B. Ordering information for sol-gel templating equipment

Item	Ordering Code	Vendor	Price ($)
Electric stir plate	11-497-6A	Fisher	290
Magnetic stir bar (3/8")	14-511-98A	Fisher	12
Filtering flask (500 mL)	10-180E	Fisher	Six for $117
Neoprene adapter	10-184-4	Fisher	12 for $46
Büchner funnel	10-356D	Fisher	36
Filter paper	09-790-12C	Fisher	100 for $6
Programmable muffle furnace*	10-650-14	Fisher	2479
Injection port kit	10-550P	Fisher	30
Porcelain crucibles	07-965D	Fisher	72 for $235

* A standard furnace can be used with manual operation; see text

C. Ordering and vendor contact information for emulsion polymerization and sol-gel templating chemicals

Prices often vary by company, product size, shipping requirements, and order date. Aldrich is generally the least expensive source, and has the largest selection of chemicals.

Aldrich
P.O. Box 2060
Milwaukee, WI 53201
1-800-558-9160
www.sigma-aldrich.com

8. Acknowledgment

9. References

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