

An Evaporative Co-assembly Method for Highly-Ordered Inverse Opal Films

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ABSTRACT

Colloidal self-assembly holds promise for photonic applications as a solution-based, low-cost alternative to top-down photolithography, if significant control of uniformity and defects can be achieved. Herein we demonstrate a new evaporative co-assembly method for highly-uniform inverse opal thin films that involves the self-assembly of polymer colloids in a solution containing a silicate precursor. Nanoporous inverse opal films can be made crack-free and with highly uniform orientation at the *cm* scale. The silicate between the colloids appears to increase the strength against cracking. This control of defects makes this method well-suited for the low cost fabrication of such films as sensors and photonic devices.

Keywords: colloid, self-assembly, inverse opal, photonic crystal, silica

1. INTRODUCTION

Self-assembly methods have proven to be undeniably important for the synthesis of nanoporous solids impossible by conventional top-down methods. Nanoporous inorganic networks have been synthesized using a variety of self-assembled organic templates. Examples include self-assembled supramolecular and colloidal templates to direct the structure of sol-gel oxide precursors, to produce mesoporous and ‘inverse opal’ materials¹⁻⁶. Such ordered, high surface area, nanoporous networks are important for the range of useful applications that such materials can find, in fields from catalysis to tissue engineering, drug delivery, gas sensing, filtration and photonics⁷⁻¹⁰. In particular, periodic inverse opal structures have been demonstrated to have 3D photonic band gaps, with sufficient refractive index contrast^{6, 11, 12}. However, the control of defects remains a persistent problem associated with bottom-up self-assembly, compared to conventional top-down methods fabrication.

Colloidal crystals themselves can be produced by methods such as sedimentation¹, shear flow⁴, and evaporative¹³⁻¹⁵ or ‘flow controlled’ deposition^{16, 17} of films on a substrate. Inverse opal structures combine a high degree of interconnected porosity (~ 75%), with highly-uniform pore size (achieved through colloidal size monodispersity).

The conventional synthesis of inverse opal materials involves the infiltration of a matrix material around a sacrificial template *after* its self-assembly^{2, 3, 6, 10, 12}, as illustrated in **Figure 1**, before removal of the template. There are two steps associated with (1) colloidal crystal assembly (such as PS or PMMA) as a template, and (2) infiltration of a sol-gel solution, before (3) removing the template to produce an inverse inorganic porous structure. This method has been used for a wide range of inverse opals, such as SiO₂, TiO₂, and Al₂O₃, using solution sol-gel precursors such as metal alkoxides^{1, 4}, the infiltration of nanoparticles¹⁶, or by deposition from a vapor phase^{11, 18, 19}. Herein we demonstrate the *co-assembly* of a sacrificial template with a matrix material to combine these two stages.

This conventional infiltration method does produce highly-ordered structures at small scales, but produces a number of defects such as cracks, domain boundaries and overlayer coatings at larger length scales². For the formation of inverse opal films it is generally difficult to achieve structural uniformity over length scales beyond ~50 μm due to under- or over-infiltration, which causes either structural collapse and cracking, or the overlayer formation. Cracking also often results due to the high capillary forces associated with the infiltration of a liquid into the high-curvature pores of the fragile colloidal crystal. Vapor phase deposition (ALD) avoids the problems of liquid infiltration, but is time consuming and expensive^{11, 18, 19}. Some efforts have been made to increase the strength of the template using partial sintering of the colloidal crystal²⁰, the growth of necks between spheres^{21, 22}, or to use a more gentle method of sol-gel infiltration¹⁷. In addition, efforts have been made to control the cracking²³ and domain orientation of colloidal crystal films through control of the evaporative deposition conditions^{15, 24}, pre-sintering of the particles²⁵, and deposition onto

topologically-patterned substrates²⁶. Ultimately, however, there have been no reliable methods to produce inverse opal films that are crack-free and with large domains over significantly large areas.

Herein, we have developed a simplified one-step, co-assembly process to combine the colloidal and sol-gel self-assembly using evaporative deposition to produce highly-ordered inverse opal films over large areas. The evaporative deposition of colloidal crystal films involves a vertically-oriented substrate that allows the self-assembly of the colloidal particles at the meniscus^{13, 14, 27}. **Figure 2a** shows a schematic illustration of a substrate suspended vertically in a colloidal suspension, to cause the deposition of a colloidal crystal film. The evaporative co-assembly method involves the deposition of polymer colloidal particles with a silica sol-gel addition, to produce a SiO₂ matrix distributed in the interstitial space of the PMMA particles (**Figure 2b**). Previously Wang *et al.*²⁸ added tetraethoxysilane (TEOS) to a SiO₂ colloidal suspension to form SiO₂ necks between spheres as a means of reducing cracking, though the necks were later etched away. Otherwise there has been no previous account of colloidal self-assembly directly with sol-gel precursors in solution.

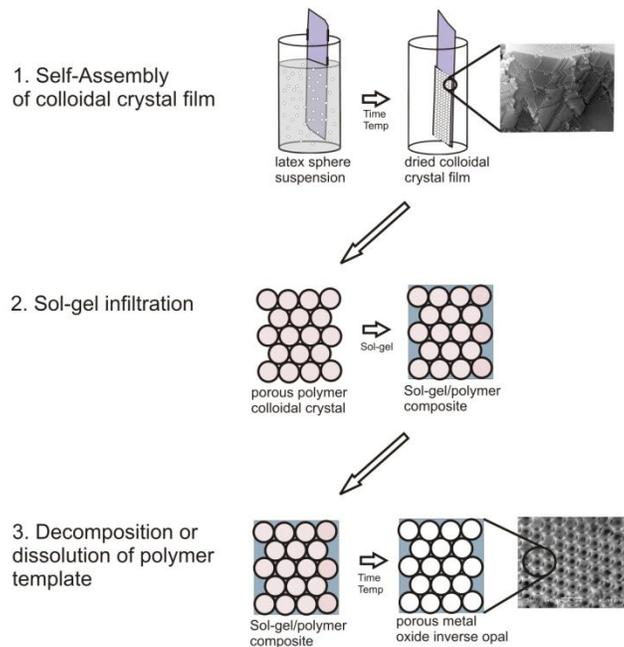


Fig. 1. Schematic of conventional method of colloidal crystal self-assembly, infiltration with a sol-gel matrix, and removal of the template to produce an inverse opal film.

2. EXPERIMENT

Colloidal particles of PMMA or PS were synthesized by emulsion polymerization, using an ammonium sulfate initiator, or purchased commercially (IFC Invitrogen). A glass or Si substrate, $\sim 1 \times 4$ cm and cleaned in piranha solution, was vertically suspended in a vial containing a 20 mL volume of 0.5 – 3.0 vol% colloidal suspensions (Figure 2a). The suspensions contained X mL of added hydrolyzed TEOS solution, where X was varied from 0 to 0.50 mL. The TEOS solution consisted of 1:1:1.5 ratio by weight of TEOS (98% Aldrich), 0.10 M HCl, and EtOH (100%), respectively, stirred at room temperature for 1 h prior to use. The colloidal/TEOS suspension was allowed to evaporate slowly over a period of 1-3 days in a 65°C oven on a pneumatic vibration-free table, to allow the deposition of a thin film onto the suspended substrate. The films were calcined in air at 500°C for 5 h, with a 4 h ramp time (Thermo Scientific).

Optical spectra were taken using a microscope-based fiber optic spectrometer system (Ocean Optics USB2000+, 300-800 nm range) on a Leica DMRX microscope using a 10x objective. Film structures were imaged by SEM (Zeiss Ultra) at 10 kV after Pt/Pd-sputter coating.

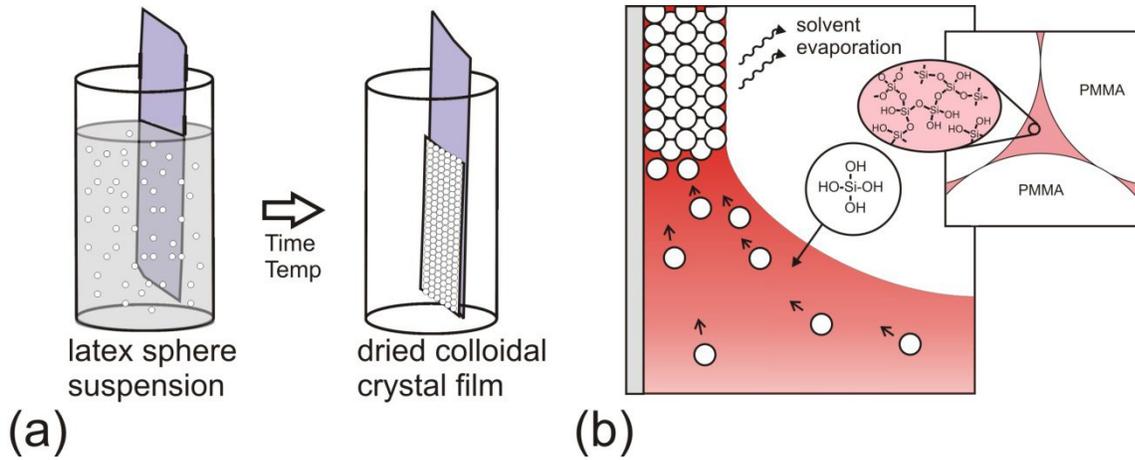


Fig. 2. (a) schematic of evaporative deposition of a colloidal crystal film, (b) illustration of the co-assembly method of colloidal self-assembly in the presence of a silicate sol-gel solution to make a polymer/SiO₂ composite structure.

3. RESULTS

An optimal SiO₂/colloid ratio was determined by adding increasing amounts of TEOS solution to the colloidal suspension. **Figure 3a-d** shows the results for a SiO₂ inverse opal film on a glass slide (after calcination at 500°C) having a 0.15 mL TEOS/20 mL colloid ratio, which produces films that can be made crack-free across the entire substrate length (ie; 2-3 cm long in these experiments). The film in **Figure 3** is a highly-uniform, crack-free film from the co-assembly of 280 nm PMMA spheres (vertical deposition direction, from top to bottom). **Figure 3a** shows an optical picture of the film showing the distinct, uniform color due to the optical interference. **Figures 3b and 3c** show that there is a face-centered cubic (FCC) structure, with the {111} plane oriented parallel to the surface, as expected for evaporative deposition^{15, 27, 29}. These films have no overlayer coating, which means that the extremely high porosity of the films is entirely accessible from the top surface. This property of the films is very important for applications such as catalysis, gas adsorption, or tissue engineering, and is not easily achieved using conventional infiltration methods^{1, 2, 5}. The TEOS/colloid ratio controls the film structure and defects. Insufficient silicate additions do not allow the formation of a continuous SiO₂ network around the colloidal template, which causes significant cracking (ie; ‘tearing’). The SiO₂ additions appear to act as a ‘glue’, and at a critical amount of the TEOS addition, there is sufficient SiO₂ matrix to allow the formation of highly-ordered, crack-free films. Cracking of opal and inverse opal films often occurs upon drying due to a combination of dehydration, polymerization-induced contraction, and local capillary forces^{23, 30}. Colloidal crystal films constrained on fixed substrate are generally too weak to resist such tensile stresses.

Increasing the TEOS content in the suspensions beyond the ideal ratio (ie; the films in Figure 3) caused the initial formation of an overlayer, which continued to thicken with larger TEOS additions. The colloidal volume fraction (for constant TEOS/PMMA ratio) determines the thickness of the films, which varies linearly with concentration.

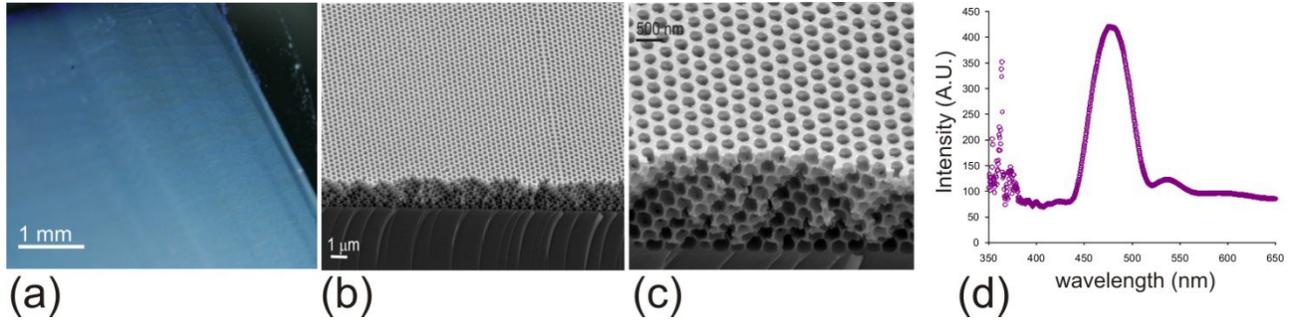


Fig. 3. SiO₂ inverse opal film after 500°C calcination, (a) optical photograph, (b) and (c) scanning electron microscopy (SEM) images of film in fractured cross-section, (d) optical spectrum measured in reflectance.

Finally, Figure 3d shows the optical spectrum of the SiO₂ inverse opal film, measured in reflectance, showing a well-defined Bragg peak at around 480 nm. The position of the first stop gap (λ_{111}) for the {111} planes, which can be simply represented by

$$\lambda_{(111)} = 2 \cdot d_{(111)} \cdot \sqrt{\langle \epsilon \rangle - \sin^2 \theta} \quad [1]$$

where $d_{(111)}$ is the d-spacing of the {111} planes, θ is the incidence angle, and $\langle \epsilon \rangle$ is the volume averaged dielectric constant of the composite, given by,

$$\langle \epsilon \rangle = V_{SiO_2} \cdot \epsilon_s + (1 - V_{SiO_2}) \cdot \epsilon_b \quad [2]$$

where V_{SiO_2} is the filling fraction of silica, and ϵ_s and ϵ_b the dielectric constant of the spheres and the background, respectively.

4. CONCLUSIONS

In summary, we have demonstrated a novel co-assembly method for colloidal self-assembly with a sol-gel precursor in solution, for the fabrication of highly uniform SiO₂ inverse opal films. The major advantages of this co-assembly process are; (1) the great reduction in defects, and cracks in particular, (2) formation of large domains, (3) there is typically no formation of an overlayer coating, and finally (4) fewer steps are involved, as a time/cost saving to the conventional method of post-assembly infiltration. There is an important advantage in being able to combine the functionality of metal oxides with the highly porous structures, at the 10¹-10³ nm length scale, associated with inverse opals. There are a number of important applications for these kind of porous, metal oxide, thin films: catalysis, tissue engineering, gas sensors, biological sensors, photonics and optical display, solar cell, drug delivery, fuel cell membrane. It will be important to explore the application of this method to other sol-gel precursors, for high refractive index materials such as TiO₂, and also for the deposition of such inverse opal films onto topologically-patterned substrates. As a result, this method could find relevance for the fabrication of waveguides or sensors for photonic or optofluidic applications.

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