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Charge stabilized crystalline colloidal arrays as templates for fabrication of non-close-packed inverted photonic crystals

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ABSTRACT

We developed a straightforward method to form *non-close-packed* highly ordered fcc direct and inverse opal silica photonic crystals. We utilize an electrostatically self assembled crystalline colloidal array (CCA) template formed by monodisperse, highly charged polystyrene particles. We then polymerize a hydrogel around the CCA (PCCA) and condense silica to form a highly ordered silica impregnated (siPCCA) photonic crystal. Heating at 450 °C removes the organic polymer leaving a silica inverse opal structure. By altering the colloidal particle concentration we independently control the particle spacing and the wall thickness of the inverse opal photonic crystals. This allows us to control the optical dielectric constant modulation in order to optimize the diffraction; the dielectric constant modulation is controlled independently of the photonic crystal periodicity. These fcc photonic crystals are better ordered than typical close-packed photonic crystals because their self assembly utilizes soft electrostatic repulsive potentials. We show that colloidal particle size and charge polydispersity has modest impact on ordering, in contrast to that for close-packed crystals.

1. Introduction

The last two decades has seen the emergence of the important field of photonic crystals. The name photonic crystals was coined to describe materials which control light propagation through periodic variations in their optical dielectric constants [1–3].

Photonic crystal materials are of major technological significance in areas such as optical computing and communications where photonic devices are being developed to replace electronic devices [3–9]. Photonic crystal materials also offer the possibility to fabricate complete three-dimensional photonic bandgap materials which exclude electromagnetic radiation (including the vacuum field) within its finite spectral bandgap [10,11]. Phenomena such as spontaneous emission are suppressed in these materials [2,12].

Lithography is the most straightforward method to fabricate two- and three-dimensional photonic crystal materials for photonic applications [13–21]. This top down fabrication methodology is highly successful in fabricating complex photonic crystal materials. These fabricated structures are extremely useful in demonstrating proof of concept for photonic crystal devices. However, lithographic processes are expensive, and this cost is likely to prevent commercialization of many photonic crystal devices.

Thus, much of the recent work in photonic crystal fabrication has utilized colloidal particle self assembly. The utility of colloidal particle self assembly is evident from the photonic crystal materials found in nature. For example, earth mined opals are photonic crystals formed from the close-packed self assembly of silica colloidal particles [22]. The first work fabricating artificial opals used gravity sedimentation to obtain photonic crystal periodic structures [23–25].

Much of the recent colloidal particle self assembly work has emphasized methods that form close-packed photonic crystal materials. These methods utilize variances of vertical colloidal particle deposition methods [26–30]. Many of these close-packed assembly methods claim formation of fcc crystals [25,31–33] which require that the self assembly select for the fcc crystal form, rather than the random stacked crystal forms. This favoring of the fcc structure appears to result from shear forces that favor fcc packing.

A major limitation of close-packed photonic crystal systems is that their ordering, and therefore their photonic crystal properties depend upon the colloidal particle size polydispersity. Clearly, increasing size polydispersity will degrade ordering [34]. Further, charge polydispersity will degrade ordering to the extent that electrostatic interactions are involved in the close packing mechanism. Disorder in the photonic crystals degrade the magnitude and increase the widths of the Bragg diffraction peaks [34–36].

Fabrication of a complete three-dimensional photonic bandgap material requires specific crystal structures and a very large periodic variation in its optical dielectric constant. The most straightforward approach to forming a complete three-dimensional photonic bandgap crystal would utilize an inverse opal fcc crystal structure that re-

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quires a minimum refractive index ratio of 2.8 [37]. The inverse opal structure is formed within an fcc photonic crystal by infiltrating an fcc photonic crystal structure with a high refractive index material, and then removing the original fcc spheres, leaving an inverse fcc lattice of air holes with a refractive index of $n = 1$.

Optimization of the inverse opal crystal structure would permit finding optimal volume fractions to increase the stop bands in particular directions [38,39].

The recent work which has attempted to generate non-close-packed photonic crystals has utilized thermal sintering and etching of close-packed colloidal crystals [40–42]. This work has also employed conformally backfilling [38,43,44] these close-packed colloidal crystals. It should be noted that the resulting photonic crystal materials retain the disorder present in the original close-packed crystals.

In the work here we demonstrate a straightforward method to form *non-close-packed* highly ordered fcc direct and inverse opal silica photonic crystals materials. We show that size and charge polydispersity has surprisingly little impact on ordering for colloidal particle systems that are formed through electrostatic self assembly. Our group has utilized the high ordering of electrostatically self assembled crystalline colloidal array (CCA) photonic crystal materials since the mid-1980's [45–50].

More recently we polymerized a hydrogel around electrostatically self assembled CCA to form a polymerized CCA (PCCA). This PCCA is a responsive photonic crystal material [51] which proved useful for chemical sensing [52–57], as well as for sensing temperature [58,59]. We also developed magnetically responsive superparamagnetic and ferrimagnetic photonic crystal materials [60–62], as well as, photonic crystals that respond to light as optical switching materials [63–67].

Electrostatic CCA self assembly relies on the electrostatic repulsions between colloidal particles of like charge. For the systems used here the colloidal particle surface groups are strong acid sulfonic acids which ionize in aqueous environments. For low ionic strength aqueous solutions the electrostatic interactions are large and occur over long distances (~1 μm) which enable formation of macroscopic fcc CCA crystals. The ordering appears superior to that which can occur for close-packed crystals because soft electrostatic potentials allow crystal annealing and they should ameliorate the disorder penalty for particle size and charge polydispersity.

Here we describe the fabrication of new highly ordered photonic crystal materials that utilize electrostatic CCA self assembly to form a highly ordered template. We then form a soft photonic crystal material where we lightly crosslink a hydrogel around the CCA template. We then condense solid silica within the PCCA hydrogel. This allows us to control the photonic crystal periodicity independently from the diameter of the colloidal particles making up the fcc crystal. This also allows us to tune the form of the dielectric constant modulation of the photonic crystal separate from its periodicity. We also demonstrate that we can remove the organic polymer and form an inverse opal structure. Thus, we can independently vary the periodicity and the silica wall thickness.

We show that our simple, electrostatic self assembly process gives rise to a photonic crystal with higher ordering compared to typical close-packed photonic crystal structure. We use DLVO theory to model interparticle interactions to gain insight into why electrostatic self assembly results in high order.

2. Experimental methods

2.1. Materials

2,2-Diethoxyacetophenone (DEAP, 98%, Acros Organics), polyethylene glycol dimethacrylate 200 (Polysciences Inc.), 2-hydroxyethyl acrylate (98%, Polysciences Inc.), diethylene glycol (Sigma), anhydrous ethyl alcohol (Pharmco Inc.) and tetraethyl ortho silicate (TEOS, Fluka) were used as received. Fig. 1 shows our synthetic scheme for fabricating an inverted photonic crystal (IPC) structure by using a CCA template.

2.2. Preparation of PCCA

The highly charged, non-cross-linked, monodisperse polystyrene colloids (Fig. 1) used to fabricate the siPCCA were prepared by emulsion polymerization [68]. The colloidal particle size as measured by TEM is 180 nm ± 4 nm. The colloidal particles were cleaned by dialysis against deionized water followed by shaking with mixed bed ion-exchange resin (Bio-Rad AG501-X8 (D)) In a typical PCCA recipe 2,2-hydroxyethyl methacrylate (6 g, 4.6×10^{-2} mol, Polysciences) and polyethylene glycol dimethacrylate (0.174 g, 5.3×10^{-4} mol, Polysciences) were mixed together in a 2 dram vial. Aluminum oxide was added to remove the inhibitor contained in the monomer solutions. The solutions were centrifuged for 5 min to remove the aluminum oxide. The deinhibited monomer solution (0.5 g) supernatant was added to 2 g of the cleaned, highly charged colloidal particle dispersion.

The resulting mixture was shaken for 30 s. Ten Percent of diethoxyacetophenone (DEAP; 10 μL, 3.84 μmol; Aldrich) was added to the mixture which was then vortexed for 30 s. The mixture was injected between two quartz plates separated by a 125 μm Parafilm spacer. UV-photopolymerization was performed by using two UV mercury lamps (Black Ray) for 13 min. The PCCA film was removed from the quartz cell and equilibrated in a deionized water bath.

2.3. Infiltration of sol–gel precursor

A silica sol–gel precursor solution was prepared using a 1:1:3 M ratio of TEOS/EtOH/water adjusted to a pH of 2 with concentrated HCl. The fabricated PCCA film template was immersed into 2 ml of the precursor solution.

Polymerization and condensation of the TEOS occurred around and within the PCCA hydrogel matrix over the course of 5 days, generating an alcogel within the PCCA template. The silica network was allowed to age and strengthen for an additional 5 days before further processing.

2.4. Solvent removal

The silica sol–gel infiltrated PCCA was solvent-exchanged for 1 week in ethanol. This ethanol-containing, silica-infiltrated PCCA (siPCCA) was then heated at 85 °C for 1 day, followed by heating to 150 °C for 5 h to remove all solvent.

2.5. Polymer removal

After solvent removal, the temperature was increased to 250 °C and held for 6 h to melt the polystyrene colloidal particles as shown in Fig. 2. Higher temperature treatment at 450 °C removed all organic polymer materials, leaving behind only the infiltrated silica [69]. Upon firing the sample cracked into small fragments consisting of monoliths approximately 2 mm on a side.

2.6. Physical measurements

Transmission electron microscopy was used to measure particle size. We used a Phillips FEG XL-30 FESEM operating in the ranges of 10–50 keV to image the inverted structures. Diffraction spectra were obtained at room temperature using an Ocean Optics USB2000 spectrophotometer with a six-around-one reflectance