Towards Photonic Ink (P-Ink): A Polychrome, Fast Response Metallopolymer Gel Photonic Crystal Device

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Summary: We demonstrate here a new kind of planarized and oriented colloidal photonic crystal device whose optical stop-band position, width and intensity can be reversibly redox and solvent tuned over a broad wavelength range by an anisotropic expansion of the photonic lattice. The material is composed of silica microspheres in a matrix of crosslinked polyferrocenylsilane[1], a metallopolymer network with a continuously variable state of oxidation[2]. Optical data was fitted using a scalar wave approximation, with a congruence to experimental data, allowing facile extraction of information concerning polymer swelling behaviour. The chemomechanical polychrome optical response of the material was exceptionally fast, attaining its fully swollen state from the dry shrunken state on a sub-second time-scale.

Keywords: colloids; gels; photonic crystals; polyferrocenylsilanes; swelling

Introduction

Photonic crystals are a class of materials which interact with electromagnetic radiation through a periodic spatial modulation in their refractive indices, when this periodicity coincides with the scale of the radiation wavelength[3-4]. These materials can easily be assembled *via* the self-assembly of a collection of monodisperse spherical colloids into a long-range ordered lattice of well-defined geometry. Spherical colloids of both inorganic and polymeric composition have been studied extensively[5], can be routinely obtained as monodisperse suspensions, and are relatively inexpensive to produce. Recent success in assembling these colloids into face-centered cubic (fcc) crystals with very low defect concentration have thrust them to the forefront of photonic crystal research [6,7].

Since many materials have been incorporated into these architectures through templating approaches[8], research has begun to focus on systems capable of being tuned in a variety of ways by external stimuli[9]. One of the ways in which colloidal photonic crystal properties can

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be tuned is *via* a mechanical response, that is changing external conditions such that the crystal changes in shape or dimensions. Previous studies have experimentally demonstrated this concept by fixing in a hydrogel matrix an array of highly charged latex spheres assembled through mutually repulsive electrostatic interactions in a rigorously deionized medium[10]. These so-called polymerized crystalline colloidal arrays (PCCA's) could take advantage of the well-known swelling properties of acrylamide-based gels[11], as well as perform sensing functions by incorporating receptors for specific analytes[12]. However, factors such as poor mechanical stability due to high solvent content, slow response to stimuli, and the polycrystalline nature of the samples, which prevents one from accurately controlling features of the Bragg peak such as frequency, width and intensity, may be stumbling blocks for their implementation into optical devices.

Silica-Polyferrocenylsilane Gel Composite Photonic Crystals

PFS is a polymer whose main chain is composed of alternating substituted silicon atoms and ferrocene groups connected at the 1- and 1'- positions of the cyclopentadienyl (Cp) rings. Thermal ring-opening polymerization (ROP) of strained, ring-tilted [1]-silaferrocenophanes affords high molecular weight polymer[13]. The monomer used here was (ethylmethyl)sila-[1]-ferrocenophane[14] unsymmetrically substituted at silicon, avoiding the possibility of micro-crystallization within the polymer network. The crosslinker was sila(cyclobutyl)-[1]-ferrocenophane, constituted of two strained rings, both of which can be ring-opened thermally[15].

The procedure and materials used to fabricate the samples have been recently described[[16]]. In essence, colloidal crystal films of silica spheres [17] on glass substrates were synthesized by an evaporative deposition method[18]. Following surface treatment, the films were infiltrated with a mixture of monomer and crosslinker and thermally polymerized to yield the desired silica-PFS composite colloidal crystal film. In the dry state these samples are extremely stable, and can be handled without any special precautions. A cross-sectional SEM image of one of the samples is shown in Figure 1.

Optical properties of both dry and solvent swollen samples in transmission mode were measured in a standard IR cell mount, which allowed for injection and removal of solvent. The peaks investigated represent selective reflection of a narrow band of wavelengths due to Bragg diffraction from the (111) crystal planes of the colloidal photonic crystal. In order to estimate the effect of the swelling on the structure of the colloidal photonic crystal, the results

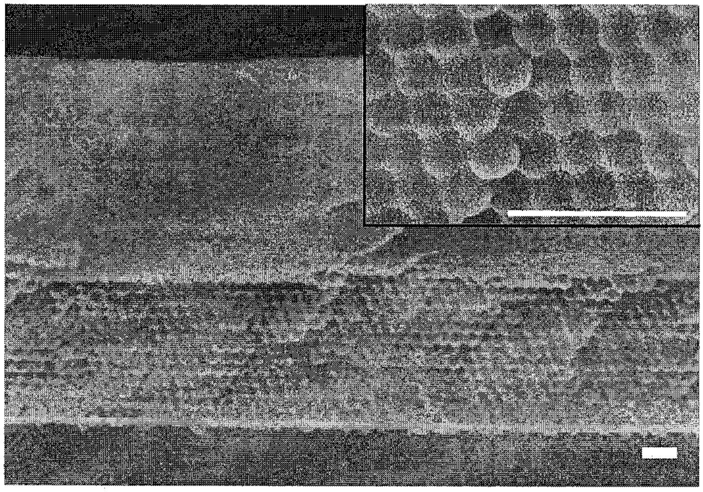

Figure 1. Scanning Electron Micrograph (SEM) image of a cross-section of the PFS-silica composite colloidal crystal film. Both scale bars represent 1 μm.

of the optical characterization were analyzed employing a theoretical model based on a scalar wave approximation[19]. This simple model has been proven to be valid to describe the transmittance and reflectance of finite size photonic crystals at the spectral region corresponding to that of the lower energy photonic bands such as the ones we investigate here[20,21,22,23]. In our case, knowing the refractive index of both the silica microspheres and the infiltrated cross-linked polymer, n=1.425 and n=1.65 respectively[24,25], as well as that of the solvent we are able to obtain the increase of the (111) interplanar distance $d_{(111)}$ resulting from the swelling process. We take into account the variation of the refractive index of the colloidal photonic crystal interstitial sites due to incorporation of the solvent to the polymer network when the swelling occurs, as well as include the presence of a substrate (glass slide) and a superstrate (polymer excess) of different refractive indices[26]. By using this approach, simulated transmission spectra were fitted to the experimental ones considering $d_{(111)}$ as the only adjustable parameter. In doing so, we reproduce the particular optical features observed for each one of the solvents, such as reflectance peak position, width, and intensity. Both the model and the experiment show explicitly how it is possible, by choosing the appropriate pair of solvents, to modulate the width of the photonic stop band keeping the spectral position of the maximum constant. For instance, both chlorobenzene and carbon disulfide swollen samples display a stop band with a spectral maximum of 843nm, but the width is varied from 13 to 15% (respectively). This is a consequence of the dual character of the tuning process. On one hand, the distance between microspheres increases during the swelling, which enlarges the lattice constant and simultaneously decreases the filling fraction of the silica microspheres in the structure. On the other hand, the refractive index contrast between microspheres and background is modified as a result of the incorporation of the solvent into the polymer network.

To demonstrate how this system allows the determination of swelling behaviour of the matrix material, the values of $d_{(111)}$ attained from this simulation were plotted *versus* the solubility parameter (δ_s) of various solvents. The greatest obtained degree of swelling results in a 21% increase in the lattice constant of the composite colloidal crystal. The solubility parameter is a numerical value empirically describing the solvent behavior of a specific solvent[27]. The obtained plot shows a maximum value of $d_{(111)}$ at δ_s=19.5, and these results are in good agreement with those obtained using a weight-difference technique on a similar polymer[12]. The straightforward analysis by the scalar wave approximation of these types of planarized photonic crystals could conceivably by used to quickly and accurately measure this important physical property for a wide range of polymers.

A kinetics experiment was conducted to evaluate the chemo-mechanical response time of the polymer-silica colloidal photonic crystal nanocomposite upon exposure to solvent. The results of the experiment are shown in Figure 2. In order to determine when the sample had reached its fully swollen state, the maximum in intensity of the first Bragg peak of the swollen sample was first noted. This wavelength was then monitored with respect to time, and carbon disulfide was injected into the cell. Before injecting the solvent, the absorbance value was low since a background had been taken of the dry sample, and this value was constant from 0 to 7 seconds. We see then a brief increase, which is due to scattering by the air-liquid interface created by the solvent rising in the sample cell and crossing the incident beam. Next, we see a sharp drop in absorbance due to a decrease in refractive index contrast between the fluid content of the cell (solvent instead of air) and the quartz plates ($n_{quartz}/n_{air}=1.54$; $n_{carbon\ disulfide}/n_{quartz}=1.06$), as well as with the glass substrate ($\Delta n_{old}=1.45$; $\Delta n_{new}=1.12$) and PFS superstrate ($\Delta n_{old}=1.65$; $\Delta n_{new}=1.01$). This decreases the light reflected at these interfaces and results in more light reaching the detector. After this increase in transmitted light intensity we see a rapid decrease representing the swelling event, after which the sample attains a constant steady state transmittance value. The whole process, from initial injection of solvent onto the dry polymer-silica colloidal photonic crystal sample to the completely swollen state, occurs in 0.4 seconds. We believe this value is a lower limit for the swelling process, and preliminary results using a Fourier-transform CCD array spectrometer indicate an optical response within 50 milliseconds of exposure to solvent with crude non-optimized solvent injection. Although we were impressed by the response speed of our materials, a fast response could have been expected given the proportionality of swelling time for polymer gels to the inverse square of the smallest dimension of the gel[28], which in our case is microscale. We were able to easily and reproducibly synthesize these materials in a very thin form which confers to them speed due to their size. In addition, we believe that the washing out of unpolymerized oligomers from the polymer network creates a certain amount of microporosity in the gel (not visible by SEM) which would reduce its effective dimensions and lead to an improvement of swelling kinetics versus a bulk dense gel.

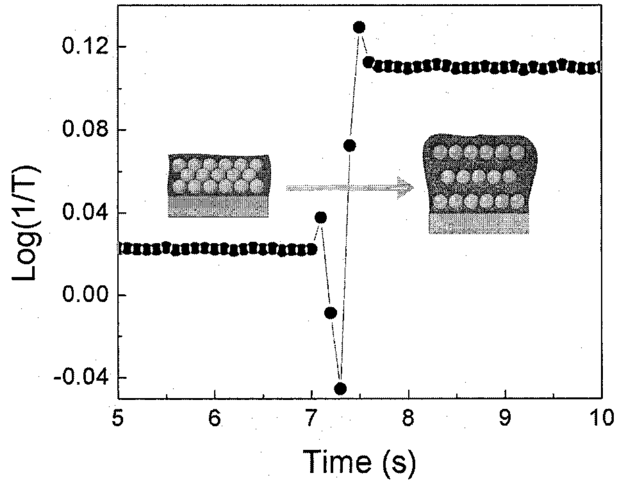

Figure 2. Kinetics plot showing the response of the silica-PFS gel composite opal upon exposure to carbon disulfide. As can be seen, the sample reaches its equilibrium swelling value within 0.2 to 0.4 seconds.

To ensure that the swelling and shrinking of these samples was indeed reversible, we conducted deswelling experiments in which the solvent was rapidly removed by application of vacuum to the flow-cell while monitoring optical properties with *in situ* optical spectroscopy.

The time required for the sample to fully deswell to its initial dimensions was comparable to the time required for the swelling process, confirming the rapid and reversible nature of the process.

Each repeat unit of PFS contains a redox-active ferrocene group, and consequently the polymer itself is redox-active. Charges on the individual iron atoms in each repeat unit can be controlled between a 0 and +1 state[29]. Therefore, PFS can have continuously variable interactions with any solvent it contacts. As an experimental demonstration of this phenomenon, the PFS-silica composite photonic crystals were subjected to multiple partial oxidations using a solution in dichloromethane (DCM) of *tris*(4-bromophenyl)aminium hexafluorophosphate (5mg/mL), a one-electron oxidant which is known to cleanly oxidize ferrocene derivatives[30]. After thorough washing and drying, the oxidized sample was swollen in carbon disulfide and an absorbance spectrum taken. From this spectrum, the degree of polymer oxidation could be estimated based on the intensity of the characteristic ferrocenium LMCT. After drying the sample, it was again oxidized, and these steps repeated until the LMCT transition no longer increased in intensity. The spectra obtained show clearly that the diffracted wavelength in the swollen state monotonically decreases with an increase in the degree of oxidation, since a charged polymer cannot be effectively solvated by a non-polar solvent. Not only can the diffracted wavelength in this system be varied between two extremes, but all intermediate states can be individually and controllably accessed.

When a sample was oxidized in the above fashion then reduced with a solution of decamethylferrocene in DCM, in was possible to obtain a spectrum virtually identical to that in the same solvent before oxidation. This not only demonstrates reversibility but also illustrates the potential use of these materials as redox sensors for species being oxidizing or reducing with respect to the redox potential of the PFS gel (tuned by the degree of oxidation) such as biologically relevant redox-proteins.

Preliminary electrochemical results indicate that when supported on a conductive substrate, this material can be repeatedly cycled between its oxidized and reduced forms within a certain degree of oxidation and in appropriate media. An electrochemical cell has been designed for this purpose, and will implemented into prototype devices such as visible light pixilated displays and near-infrared optical telecommunication switches and attenuators by using, respectively, smaller and larger spheres than the ones used in this work. A detailed spectroelectrochemical study is in progress.

Conclusion

This report demonstrates a conceptually new approach to the fabrication of rapid-response chemo-mechanical colloidal photonic crystal device with redox and solvent tunability based on the anisotropic expansion of the crosslinked PFS matrix surrounding a close-packed array of unconnected silica spheres[16]. The samples are planarized and oriented, and present a very low defect concentration, portending the use of this system in future optical communication systems and electro-photonic displays.

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