High Resolution Reversible Color Images on Photonic Crystal Substrates

Pilgyu Kang,† Samuel O. Ogunbo,‡ and David Erickson*†

†Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853, United States
‡Department of Mechanical Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States

Supporting Information


INTRODUCTION

Structural color is ubiquitous in nature and can be found in butterfly wings,7 squid skin,8 peacock feathers,9 and the spines of sea mice.10 These animals use structural color and their ability to mechanically change the local periodicity of the internal nanostructures that generate it to create adaptive camouflage8 or look more attractive to the opposite sex.9a Its success in nature has inspired the incorporation of structural color into numerous technologies including displays,4a tunable optical filters,11 and gas sensors.12 For these and other applications, numerous methods have been developed for tuning structural color including electrical actuation,13 chemical stimulus,4b light-triggered liquid crystals,14 vapor absorption,15 nanofluidics16 and mechanical strain.17

Structural color is a natural fit for new display technologies and writing substrates, since it can provide vivid colors in environments of high intensity light (e.g., sunlight) without the need for additional illuminating power. Most existing display technologies such as LCDs and LEDs require power to actively project colors and often suffer from performance degradations in these reflective environments. Recognizing this, researchers have developed a number of techniques for dynamically and spatially modulating the colors reflected off of photonic-crystal-like substrates, for example, using electrical4a and magnetic18 actuation methods. The application of these external fields to drive the color change can be fast and provide good dynamic range, but they require external power, an embedded method for spatially modulating the field, and are not directly applicable to writing substrates. Here we demonstrate an electrical-power-free infusion technique that allows us to draw multicolor images on photonic crystal substrates using transparent imaging oils. Through the use of multiol inkjet printing, we demonstrate the creation of custom images with the resolution down to 200 μm without the need for predefined template stamps.19 The substrates can be returned to their initial state through the application of erasing oil and are compatible with low cost mass production techniques.20

EXPERIMENTAL SECTION

The procedure for creating self-assembled colloidal photonic crystal (CPC) substrates can be found in earlier publications.19,21 Here the
CPC substrates are fabricated from monodisperse polystyrene (PS) nanospheres (Polysciences, Inc.) 200 nm in diameter dispersed at 25 mg/mL in pure water. Glass slides used to perform the assembly were first cleaned in 95% sulfuric acid for 1 h to remove organic residues and make surfaces hydrophilic. Next the glass slides are rinsed with acetone, 2-propanol (IPA), and DI water. To further increase the wettability, the glass slides are treated with oxygen plasma (Harrick Plasma) for 1 min. To initiate the assembly process, 3 mL of the PS dispersion solution was dispensed on the glass slides and then immediately covered with silicone oil (Gelest, Inc., polydimethylsiloxane DMS-T11, $\eta = 10$ cSt) to slow the evaporation process, enabling long-range order to be obtained. Substrates were placed in an oven at 60 °C for several days while the assembly proceeded. After the water was completely evaporated, the silicon oil was carefully cleaned off. Premixed polydimethylsiloxane (PDMS; 1:1 mixture of PDMS base (Sylgard 184) and silicon oil (Gelest, Inc., polydimethylsiloxane DMS-T00, $\eta = 0.65$ cSt)) was then poured over the substrate, allowing it to infiltrate into the interstitial spaces in the crystal.

**RESULTS AND DISCUSSION**

Figure 1a shows a sample polystyrene CPC substrate used here, in both the amorphous state (left side) and the crystalline state following completion of the self-assembly based fabrication process (right side). The substrate fabrication technique exploits the capillary forces generated during solvent evaporation to drive the self-assembly, and we embed the final crystal structure in PDMS using a technique similar to that described by Fudouzi and Xia. Details of the fabrication process are provided in the previous Experimental Section. As is shown in Figure 1b, the capillary force arranges the PS beads in such a way that they form a face-centered-cubic crystal structure so that the [1 1 0] direction is parallel to the glass substrate. The number of layers in the crystalline structure is determined by the concentration of PS beads suspended in the solvent and the overall area of the substrate. In general, our structures comprised about a hundred layers, resulting in a substrate approximately 40 $\mu$m thick. Following formation of the crystal, a liquid phase of premixed PDMS being polymerized later is infused into the voids via capillary action and solidified into the elastomeric form. Wohlleben et al. also presented similar techniques to achieve elastic colloidal crystals exploiting a mechano-optical effect rather than the chemical-optical effect demonstrated here. Our CPC substrate is fabricated on fused silica for mechanical robustness that leads to potential applications such as the fluidically writable display demonstrated in this study. Thus, in our investigation, the elastic property of the infused PDMS matrix is not the direct measure of reconfigurability as it was in that study.

For our CPCs the wavelength of the incoming light that will be most strongly reflected, $\lambda_{\text{ref}}$, can be approximated by the Bragg equation:

$$\lambda_{\text{ref}} = 2d_{\text{lat}}(n_{\text{eff}}^2 - \sin^2 \theta)^{1/2}$$

where $d_{\text{lat}}$ is the
lattice constant in the [1 1 1] direction, \( n_{\text{eff}} \) is the effective refractive index, and \( \theta \) is the angle of the incidence.\(^{21,24} \) From this equation, it can be seen that the wavelength of the light reflected from the CPC substrate is directly proportional to the lattice constant. It is noted that the wavelength of the reflected light also depends on the observation angle, since it is a function of the incident angle as in the Bragg equation above. Thus, colors observed for our CPCs are seen differently from the angle of view. Here we focus on the colors viewed at an angle of 90° with the CPC substrate for consistency. The dependency on viewing angle might limit some applications where colors must be consistent over broader viewing angles. Locally swelling the lattice therefore will cause the reflected wavelength to increase. To accomplish this here, we use a series of different silicone oils as “colorless inks”.\(^{19} \) When applied to the CPC substrate, silicone oils will diffuse into the polymerized PDMS matrix and cause it to swell,\(^{38} \) thereby increasing the interstitial distance and red-shifting the reflected wavelength (see Supporting Information Movie S1). Silicon oils with larger molecular weights (i.e., different lengths of the SiOC\(_2\)H\(_6\) monomer chain) cannot diffuse as readily into the PDMS matrix and thus tend to result in less steady state swelling than lower molecular weight variants and therefore a smaller red-shift. Figure 2a shows the reflectance spectrum obtained from an initially green CPC substrate (peak reflectance 542 nm) for the range of commercially available silicon oils (Gelest Inc., Morrisville, PA) from the high molecular weight T00 (molecular weight 3780 u) to the low molecular weight T01 (162 u). The peak reflectance wavelength for all the oils used here is plotted in Figure 2b, using both initially blue (200 nm PS beads, represented with \( \Delta \)) and green substrates (210 nm PS beads, represented with •). As can be seen in both cases a linear response between the log of the oil’s molecular weight and the reflected wavelength is obtained. This linear dependence of reflected wavelength is similar to that observed previously by Fudouzi and Xia.\(^{20} \) In addition to being transparent and providing broad tunability, silicone oils have the additional advantages of being chemically nontoxic, having relatively low viscosity, and exhibiting low volatility.

To create high-resolution images on these substrates, we make use of a Dimatix Material Printer which has the capability to deliver oils of different molecular weights and viscosities with high positional accuracy. As can be seen in the images included in the Supporting Information section S1, by adjusting the driving voltage profile applied to the piezoelectric nozzle, the size and shape of ejected droplet can be optimized. The achievable image resolution however is a function of both the droplet size and the diffusion distance within the substrate. We estimate the resolution limit of the system using a series of test patterns consisting of stripes 200 \( \mu \text{m} \) wide, 1 mm long, with spacing ranging from 100 to 500 \( \mu \text{m} \) as shown in Figure 3a. After transferring the test pattern to the CPC substrate, the intensity profile across each pattern was analyzed using ImageJ; this is plotted in Figure 3b.

We define here the minimum achievable resolution as that above which the five discrete peaks could be clearly identified. Figure 3c details the 200 and 300 \( \mu \text{m} \) spacing conditions where it can be seen that while the features blend together for the 200 \( \mu \text{m} \) case, with 300 \( \mu \text{m} \) spacing each separate feature is clearly distinguishable.

Three different images of varying complexity and color range are recreated in Figure 4. The first three images in Figure 4 show the logos of Cornell University (a, which contains fine features and letters), and Cornell Athletics (b,c) transferred to the blue CPC substrate with a monochrome green ink. Figure 4f–h shows similar images transferred to the green CPC substrate in a monochrome orange ink. The remaining images show three color image replications where the logos are separated into two different sections, with parts colored using the T03 and T11 oils, respectively. On the blue CPC substrate, this results in blue (T11), and orange (T03) images, and on the green CPC substrate this results in green, orange (T11), and red (T03) images. Although for low resolution images, the color change was instantaneous, for the high resolution images, between 5 and 7 min were required for the full image to form. This includes the time for pattern transfer and for the relatively small amount of oil to fully diffuse into the base substrate. In uncontrolled environments, the image stability is governed by the evaporation rate of the oils which in itself is dependent on the molecular weight. The oils with relatively large molecular weights created images that tended to last for several days or weeks (T15 (over a month), T05, T07, T11 and T12 (10–15 days), T02 and T03 (4–5 days)), whereas the oils with smaller molecular weights could evaporate in as little as a few minutes (T01 and T01.5 (2–3 min))

The low vapor pressure of the low molecular weight oils can be exploited to erase transferred images and the reset the substrates. The lowest molecular weight T00 silicone oil exhibited a very low viscosity, enabling it to penetrate deep into the photonic crystal structure and mix with and dilute any existing image producing oils and then promptly evaporate within a few seconds. Figure 5 shows sequential images of (a) an image displayed on the CPC substrate, the intensity profile across each pattern was analyzed using ImageJ; this is plotted in Figure 3b. We define here the minimum achievable resolution as that above which the five discrete peaks could be clearly identified. Figure 3c details the 200 and 300 \( \mu \text{m} \) spacing conditions where it can be seen that while the features blend together for the 200 \( \mu \text{m} \) case, with 300 \( \mu \text{m} \) spacing each separate feature is clearly distinguishable.
substrate, (b) the same substrate following application of the T00 oil, and (c) the original image location after evaporation of the T00 erasing oil (see Supporting Information Movie S2). As can be seen, the substrate is returned to the original color without a trace of the original image. The erasing procedure takes less than 10 s after the T00 oil is applied. We have been able to use this procedure in excess of 30 times without the degeneration of the original substrate or reduction in the quality of the reproduced images. The CPC substrate can be reused in the writing and erasing cycle without degradation unless the photonic crystal structure in the PDMS matrix is physically damaged (for example) by scratching. For potential application as a writable display, an additional PDMS layer on top of the CPC substrate could provide greater robustness. This could however increase the diffusion time for the oils and slightly degrade the image quality due to the additional diffusion distance.

**CONCLUSIONS**

In this paper, we have demonstrated the use of self-assembled colloidal photonic crystal substrates to support high resolution, multicolor, stable but erasable images printed with transparent silicon oils of varying molecular weight. We expect that such a technique could find applications in the development of new flexible and stretchable drawing substrates and low power reflective display technologies.

**ASSOCIATED CONTENT**

Supporting Information. Figure S1 and Movies S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: de54@cornell.edu.

**ACKNOWLEDGMENT**

This work was partially supported by the Air Force Office of Scientific Research through an STTR grant to Illuminaria LLC. under the Reconfigurable Materials for Cellular Electronic and Photonic Systems discovery challenge thrust and by the US National Science Foundation through grant NSF-CBET-0846489 “CAREER: Optofluidics - Fusing Microfluidics and Photonics.” This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECS-0335765). The authors appreciate access and the use of the facilities of the Nanobiotechnology Center (NBTC), an STC Program of the National Science Foundation under Agreement no. ECS-9876771.
LETTER


