From Metastable Colloidal Crystalline Arrays to Fast Responsive Mechanochromic Photonic Gels: An Organic Gel for Deformation-Based Display Panels

*Dongpeng Yang, Siyun Ye, and Jianping Ge**

An efficient and straightforward method is developed to prepare a mechanochromic photonic gel by fixing the metastable SiO_2 colloidal crystalline array (CCA) in the mixture of ethylene glycol (EG) and poly(ethylene glycol) methacrylate (PEGMA) through photopolymerization. Thanks to the recent fabrication of solvent-wrapped, metastable CCA, a high volume fraction of EG (46%) is introduced to the photonic gel before particle assembly, but not by swelling after polymerization, which leads to a more deformable composite than most reported opal gels. Compared to traditional photonic gels, this opal gel not only has improved mechanochromic sensitivity to weak external force and extended color tuning range from red to blue ($\Delta\lambda = 150$ nm), but also possesses fast and reversible response in millisecond level (20–200 ms), repeatable reflection signals in cycling and fatigue tests, and good resolution in response to localized deformation, which renders it an ideal deformation-based photonic display screen. A new trigger system is designed to solve the large deformation causing color fading in conventional mechanochromic gels and brilliant red, green, and blue (RGB) pixels can be conveniently manipulated by 'pushing' operations.

1. Introduction

Responsive photonic crystal (RPC) has aroused tremendous interests recently, because it tightly wires the external stimuli, the crystal structure and the optical signals together. The optical properties of RPC are generally determined by its lattice constant, refractive index and orientation, which are further controlled by deformation, solvent/gas infiltration and electromagnetic field, etc. Based on these relationships, the RPCs have been broadly investigated as promising materials in sensing, bio-detection, display, printing, security device, lasing, optical propagation and solar cells.[1]

Among various RPCs, mechanochromic photonic crystal is probably the earliest member in this family,[2] because it simply converts the deformation of bulk materials into the change of lattice constant and then the alteration of optical signals. Although the mechanochromic PC has already been explored to show its possible application in mechanic sensing,[3] gas pressure sensing,[4] fingerprints identification,[5] mechanical lasing[6] and fluorescence tuning[7] in the past decade, its study is still limited by the entire or partial "hard materials" forming the RPC, as mentioned by Thomas and Chan in a recent review article.[8] A more deformable photonic crystal will undoubtedly lead to larger stop-band shift with strain ($\Delta\lambda = \lambda_0 \cdot \varepsilon$) and better sensitivity in mechanochromic response. However, the flexibility and the fixing of highly ordered structure are always difficult to be satisfied at the same time no matter for one dimensional (1D) or three dimensional (3D) PCs, which makes the synthesis a big challenge for researchers.

The reported mechanochromic photonic crystals can be classified into two categories according to the dimension of dielectric periodicity (1D and 3D). 1D mechanochromic RPC can be prepared by self-assembly of cholesteric liquid crystal macromolecules in silicone elastomers.[9] It can also be prepared by self-assembly of a diblock copolymer, polystyrene-*b*-poly-2-vinylpyridine (PS-*b*-P2VP), into lamellar stacking of alternating PS and P2VP micro-domains, followed by solvent annealing in chloroform to improve the long-range order and swelling with acetic acid aqueous solution to introduce the elasticity.[3b,10] Furthermore, the elastic 1D RPC can be prepared by assembly of hydrophobic poly(dodecyl glyceryl itaconate) (PDGI) molecules into periodically separated parallel bilayers in a polyacrylamide matrix.[11] The most remarkable merit of these photonic gels is the large deformation ratio and broad reflection tuning range (~300 nm) due to the pure and soft polymer composition, but the recovery of original reflection after removing the strain is slow (~15 s) due to the same reason, which makes it unsuitable for deformation-based display panel. For fast mechanochromic response, the 3D opal structures composed of colloidal crystal array and polymer matrix actually have intrinsic advantages[12] considering the rigidity brought by the solid particles. However,

S. Y. Ye, Prof. J. P. Ge
Department of Chemistry
Shanghai Key Laboratory of Green Chemistry
and Chemical Processes
East China Normal University
3663 North Zhongshan Road, Shanghai, China 200062
E-mail: jpge@chem.ecnu.edu.cn

D. P. Yang
Department of Chemistry
Tongji University
1239 Siping Road, Shanghai, China 200092

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the optical tuning range (35~120 nm) is sometimes inadequate to cover the entire visible spectra.[2,13] It should be mentioned that almost all the reported 3D mechanochromic gels are made from polystyrene (PS) particles, which means a time-consuming de-ionization process using dialysis and ion-exchange resin in synthesis may be inevitable. The porous characteristic in reverse opal gel can improve the gel's flexibility without sacrificing the fast mechanochromic response,[5] which is a good solution to 3D system. However, the only reported gel was not perfectly durable in repeated usage as the reflection tuning range decreased after 10 cycles. People will summarize from the above survey that although the mechanochromic photonic crystal have been demonstrated before, an improved material with simple and efficient synthesis, as well as sensitive, fast, reversible and durable mechanochromic response is urgently required even now.

In this work, we reported a fast responsive mechanochromic photonic gel and revealed its superior mechanic sensitivity, response rate, reversibility, durability and resolution as a deformation based display material. The photonic gel was prepared by in-situ fixing the metastable SiO_2 colloidal crystalline array (CCA) in the mixture of ethylene glycol (EG) and poly(ethylene glycol) methacrylate (PEGMA) through photo-polymerization. The synthesis was straightforward and efficient as the SiO_2/EG-PEGMA gel can be obtained from commercial chemicals within 8 h, including synthesis of Stöber SiO_2 particle (4 h), particle purification (1 h), assembly of metastable CCA (2h) and UV curing (20 min), which greatly simplify the synthesis and improve the efficiency. Recently, we have developed a solvent wrapped metastable CCA in various organic solvent.[14] When the solvent is partially replaced by liquid monomers, the metastable CCA can be converted into fixed CCA through photo-polymerization, which makes it possible to introduce very high volume fraction of ethylene glycol (46%) into PC composite. It should be noted that this high loading of liquid content can't be achieved by pure swelling after polymerization. The pre-infiltrated solvent greatly improve the softness and elasticity of the opal gel, which makes the structure color more sensitive to the external forces and leads to a totally 150-nm reflection wavelength shift (covering red-green-blue colors) under deformation. Meanwhile, the mechanochromic gel retains the merit of 3D opal structure in framework rigidity, so that a fast and reversible mechanochromic response with stable and repeatable optical performance in cycling and fatigue tests can be achieved. The deformation and color change can be confined in a small region to produce patterns with high resolution, and the gel can topologically show the patterns on stamps without losing any details. A new deformation based display panel was designed to solve the large deformation caused color fading in conventional mechanochromic gels, and brilliant red, green and blue pixels can be conveniently manipulated by "pushing" operations only.

2. Results and Discussion

The mechanochromic PC composites were prepared by three continuous steps including 1) assembly of metastable CCA in EG and PEGMA, 2) conversion to elastic gel by photo-polymerization and 3) encapsulation in polydimethylsiloxane (PDMS) matrix. (**Figure 1**) The first step was discussed in our recent work about metastable colloidal crystalline array.[14] Typically, Stöber SiO_2 particles dispersed in ethanol were first mixed with EG and PEGMA (EG/PEGMA = 1~1.8/1) to form a homogeneous colloidal suspension at room temperature. After evaporation of ethanol at 90 °C, the liquid suspension was cooled down to room temperature to form solvent wrapped metastable CCA in EG and PEGMA. Then, the precursor was sandwiched between two glass slides and quickly converted to an elastomeric organic gel under UV irradiation. The fixing of metastable CCA inside the EG-PEGMA gel was attributed to the physical crosslinking in the presence of SiO_2 particles, since no chemical crosslinker was added here. Finally, the elastic photonic crystal gel was further swelled by EG and encapsulated in PDMS matrix to ensure repeated usage as display unit.

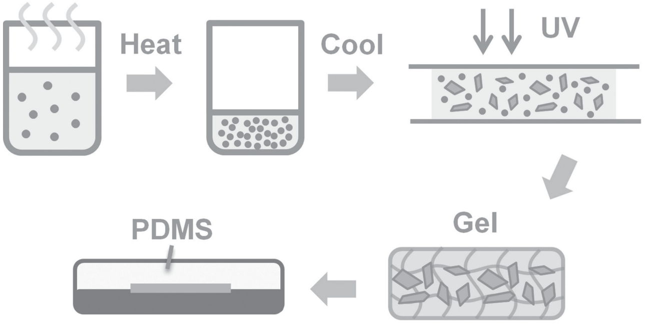

Figure 1. Scheme for the fabrication of mechanochromic photonic crystal gels.

The elastic SiO_2/EG-PEGMA photonic gel is composed of SiO_2 CCA and amorphous stacking of SiO_2 particles. Since the elastic SiO_2/EG-PEGMA gel can't be observed by SEM due to its liquid content, it was dried to remove EG first. The cross section SEM image (**Figure 2**) of the dried gel proved the existence of both crystalline and amorphous SiO_2 assemblies, which is consistent with the observation of separate microscale colloidal crystals in optical microscope image. (**Figure 3**) The

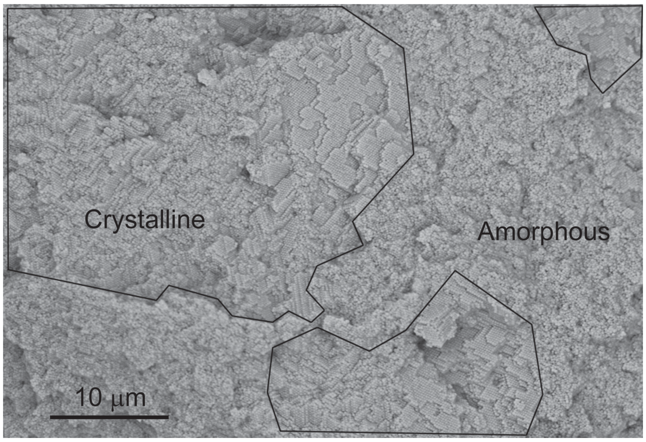

Figure 2. SEM image of the cross section of dried SiO_2/EG-PEGMA gel, which includes both the crystalline and amorphous SiO_2 colloidal assemblies.

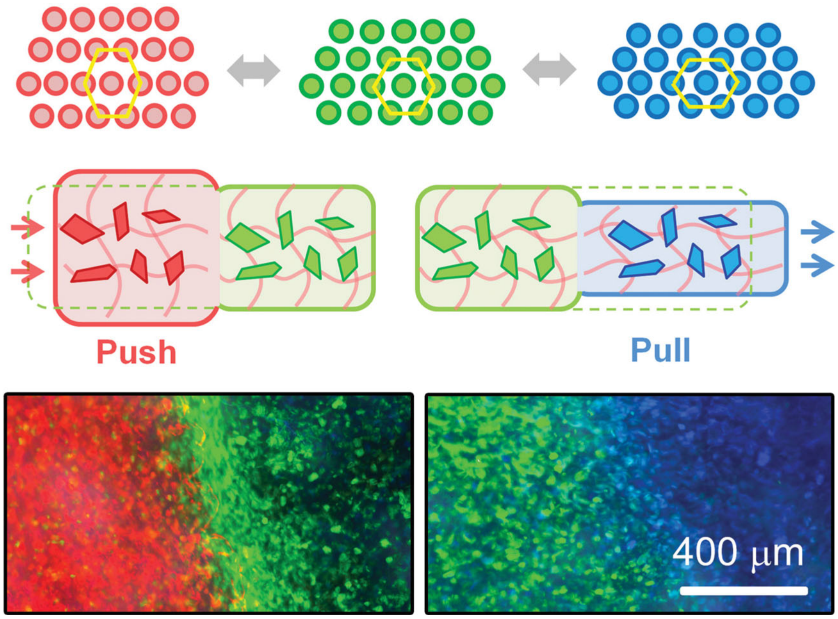

Figure 3. Optical microscope images of mechanochromic photonic crystals and illustration to their structure change under deformation.

coexistence of crystalline and amorphous zone is believed to inherit from the liquid monomer precursor where metastable CCA precipitate out of the solution. It also suggested that the polymerization fixing is effective so that both the ordered and disordered arrangement of particles were mostly retained.

Without affecting the gel formation and particle assembly, high volume fraction of EG was introduced before UV curing, which leads to a more elastic composite than most reported opal gels. It is know that PEGMA can be swelled by water and polar organic solvents such as ethanol and EG. If the colloidal crystals were first fixed in a pure PEGMA matrix and then swelled by EG to its saturated state, the as-prepared photonic gel will show limited capability in stretching due to the internal stress of physically cross-linked polymer matrix, which eventually leads to limited tuning of structural colors. However, when large amount of EG was directly added to the monomers, the as-made photonic gel will be more elastic and deformable. The volume ratio of EG and PEGMA can be increased to 2:1, where a gel still form by UV irradiation. When the gel was in original state with no internal stress at all, large interspacing between neighboring colloids gave the photonic composites adequate space for both expansion and shrinkage, so that the deformation and color tuning will be much easier. As a demonstration, a green photonic gel will turn to red or blue when part of it was pushed or pulled horizontally, which could be explained by the corresponding lattice change in vertical direction. (Figure 3) Brilliant colors of the embedded microcrystals first proved the high order degree of photonic structure and the feasibility of current assembling method. While, the sharp color changing caused by pushing or pulling suggested the elastic polymer networks could change the crystal structure effectively, which makes the materials highly responsive to the mechanical forces.

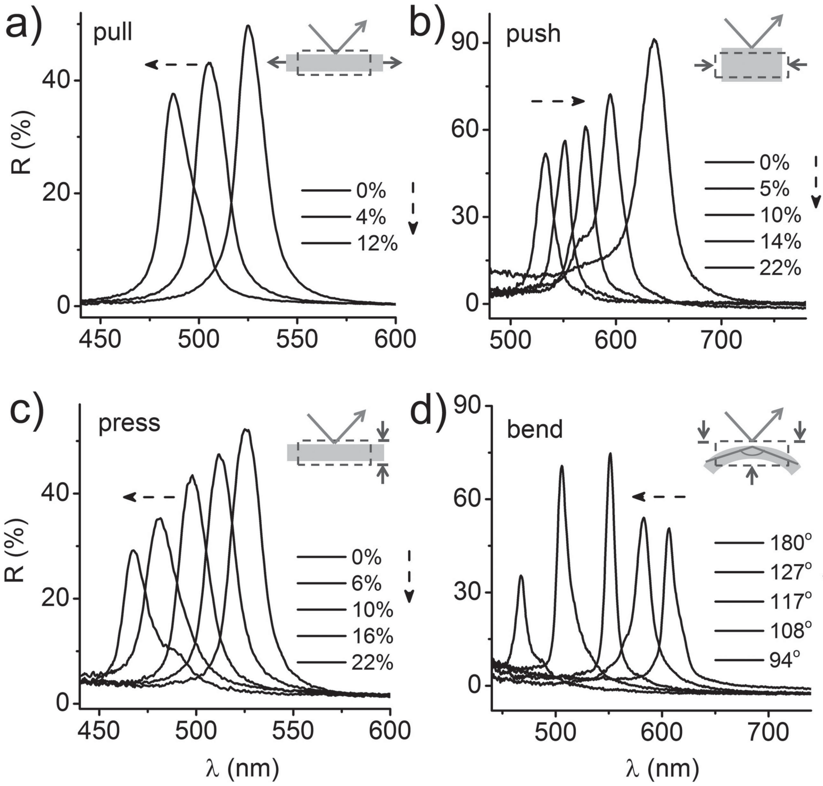

Figure 4. Optical response of elastic photonic crystal gels to simple deformations.

Simple deformations, including pulling, pushing, pressing and bending were tested to characterize the mechanochromic properties, and to seek the most effective way to induce large structure color change with current materials. Generally, the optical fiber was placed vertically above the PC film to collect the reflection signals. The three dimensions of the samples and the detailed measurement setup were introduced in the supporting information. (Figure S1, S2, Table S1, S2) **Figure 4** showed that the original reflection around 525–530 nm would blue- or red-shift to 487 and 636 nm, as the gel horizontally stretch and shrink for 12% or 22% respectively, giving a total wavelength change ($\Delta\lambda$) about 150 nm. When the photonic gel was vertically pressed to cause a 22% of decrease in thickness, its reflection blue shifted from 525 nm to 467 nm. Two

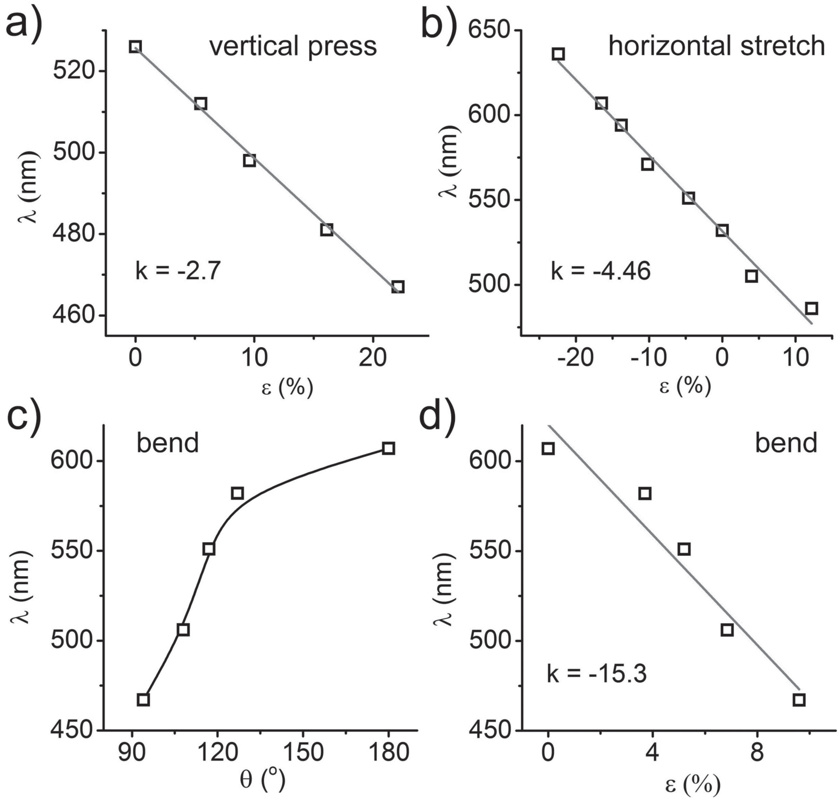

Figure 5. Linear relationship between the reflection wavelength and deformation ratio.

dimensional (2D) bending also caused the reflection blue shift from 606 to 467 nm when the gel was bended from a plane to a right-angle, giving a total Δλ of 140 nm on top of the arc. Although the gel would break as it was pulled, pushed upon 20% or bended downward 50°, the 150-nm Δλ is larger than most reported elastomeric opal or reverse opals hydrogels, which could show red, green and blue colors with one sample.

The reflection wavelength is in linear relationship with the deformation ratio (ε) in all experiments, and different slopes suggested that formation of 2D curved surface is the most effective way to create large color contrast without breaking the samples. (**Figure 5**) According to the Bragg's equation, the final λ after deformation is in proportion to the change of lattice in the orientation of incident light (ε_z), assuming the total refractive index keeps same all the time. In all the experiments above, we actually measure the apparent deformation ratio (ε_a), which is proportional but not equal to real ε_z, so that the linearity remains but the slopes are different in each experiment. For pulling and pushing, a horizontal stretching/shrinkage of photonic gel were accompanied by a compression/expansion of vertical lattice, which cause a blue/red-shift in reflection. Bending is similar to stretching, as the arc length increases along with bending, leading to a vertical compression either. These results fully confirmed the validity of the gel's mechanochromic property due to the good consistency with Bragg's Law. It should be noted that the slope of the fitted straight line actually evaluate the easiness of shifting the reflection with a same ε_a, which indicates that forming 2D curved surface by bending or 3D curved surface by poking the photonic gel might be an effective way to induce a line or spot pattern with large color change.

For a mechanochromic photonic gel serving as potential material for display or actuator, one will be very interested to know how much pressure is required to realize the color changes, how fast the switching of reflection wavelength can be, and what is the critical resolution for a localized color changes. The answers to these questions are all tightly related to the desired reflection wavelength change (Δλ). First of all, the relationship between applied pressure (P) and induced Δλ will be explored, and the detailed measurement setup was introduced in the supporting information. (Figure S3) When pressing a mechanochromic gel containing 46% of EG (Sample #4), the required pressure gradually increase from 0 to 109 kPa as the induced Δλ rise from 0 to 100 nm. (**Figure 6**) It should be noted that the volume fraction of EG was calculated according to the solvent mixed with monomer and those absorbed by swelling after polymerization. Here, we have prepared Sample #1 with no addition of EG in two processes (0% EG), Sample #2 with addition of EG only by swelling (15% EG) and Sample #3 and #4 with introduction of EG in both steps (36%, 46% EG). With the increase of liquid content, the gel becomes more deformable, so that a small pressure is adequate to achieve large Δλ. This proves the significance of EG addition in monomer again, because a saturated EG swelling of pure SiO_2-PEGMA photonic crystals only producing a gel with 15% of solvent, which has worse mechanochromic response than the typical sample. Based on the color changes and corresponding pressure (100 nm/109 kPa; 60 nm/58 kPa), the current photonic gel has better mechanochromic capability than

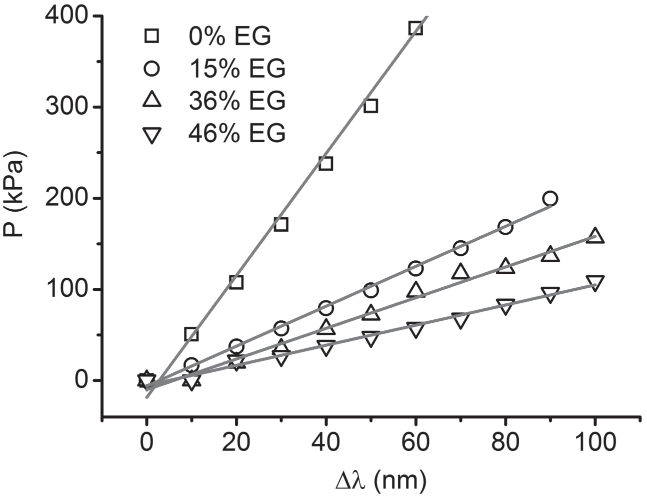

Figure 6. Relationship between applied pressure and the induced wavelength change showing how much pressure is required to realize a certain color change.

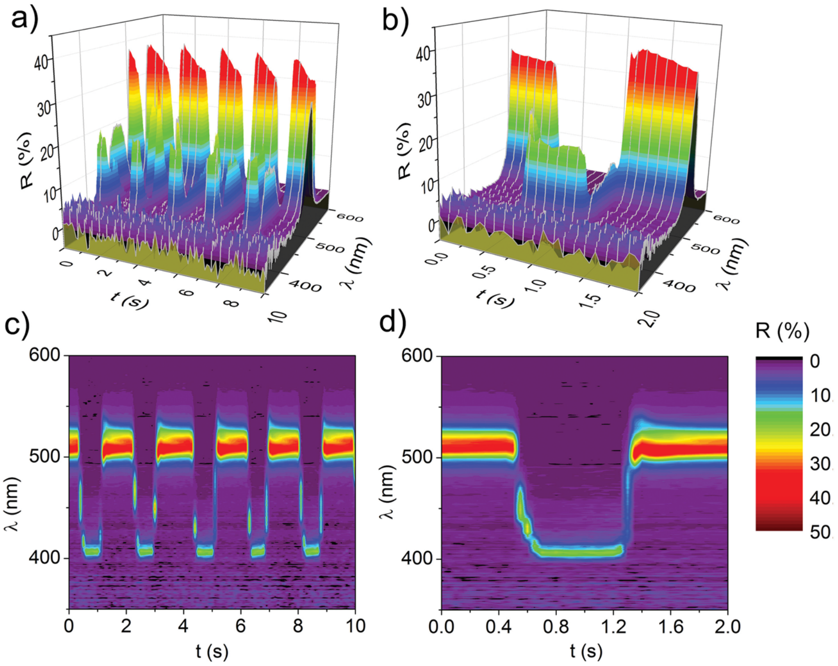

Figure 7. 3D surface map and color filled contour map showing the time evolution of reflection spectra as the gel was periodically pressed and released. The rainbow color metrics indicate the intensity of reflection peaks.

secondary polymerized opal hydrogels (93 nm/145 kPa),[12] but worse than the inverse opal structures (60nm, 15 kPa).[5] However, considering the size of a pixel, the mechanochromic effect is adequately sensitive to create a sharp and localized color change on photonic gel, as demonstrated later in this manuscript.

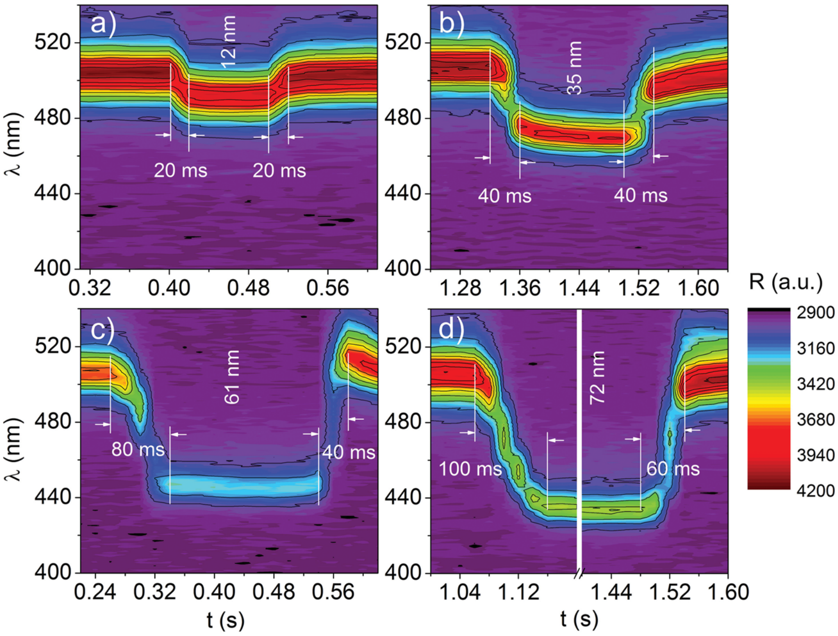

Figure 8. 3D contour map showing the response time of deformation and recovery, when the reflection switching ($\Delta\lambda$) was set to 12, 35, 61 and 72 nm. The rainbow color metrics indicate the intensity of reflection peaks.

The optical response of PC gel to mechanical force is fast and fully reversible. Here, the optical spectrometer with integration time of 50 ms was used to record the evolution of reflection spectra when the gel was periodically pressed and released for 1 s. The detailed measurement setup is introduced in the supporting information. (Figure S4) As shown in **Figure 7**, the original reflection at 510 nm quickly blue-shifts to 410 nm as the gel is pressed and it switches back as the pressing is released. It takes about 200 ms to achieve a 100-nm blue-shift upon deformation and 100 ms to recover, so the mechanochromic response is adequately fast to synchronize with the external mechanic actions at frequency of 0.5 Hz. We actually measured the reflection change in continuous 30 cycles, although only 5 of them were shown here. From 3D surface map and contour map of reflection evolution, one can find that the switching of reflection wavelength and even the intensity are highly repeatable. Thanks to the rigidity of opal structure, it has intrinsic advantages in durability comparing with the porous inverse opals, and its tuning range (100 nm) shows no decay at all after repeated tests.

The response rate can be faster when the deformation and the reflection wavelength change between original and deformed state become smaller. (**Figure 8**) According to the results in Figure 6, 100-nm shift of reflection wavelength is the maximum $\Delta\lambda$ when pressing the sample. The largest decline in response time (200 to 100 ms) takes place when the target $\Delta\lambda$ change decreases from 100 to 72 nm. As the target $\Delta\lambda$ further decreases from 72, 61, 35, to 12 nm, the mechanical response time decreases from 100, 80, 40 to 20 ms accordingly, and the recovery time decreases from 60 to 20 ms either. In other words, the mechanochromic response rate can speed up to millisecond scale if the expected color change is moderate. Sometimes, such sacrifice in $\Delta\lambda$ for response speed is acceptable for sensors and actuators, as current spectrometer can easily distinguish reflection change in several nanometers. The deformation-dependent response rate suggests that the photonic gels may undergo poroelastic relaxation,[15] which involves both the mechanical deformation and fluid transportation. When a large deformation is made or the gel recovers from a large deformation, the solvent EG will need more time to transport to its new balanced position, which causes the response time longer than the case of small deformation.

There are very few reports discussing the response time of mechanochromic PC. For example, a porous reverse opal made of ethylhexyl methacrylate can instantly show

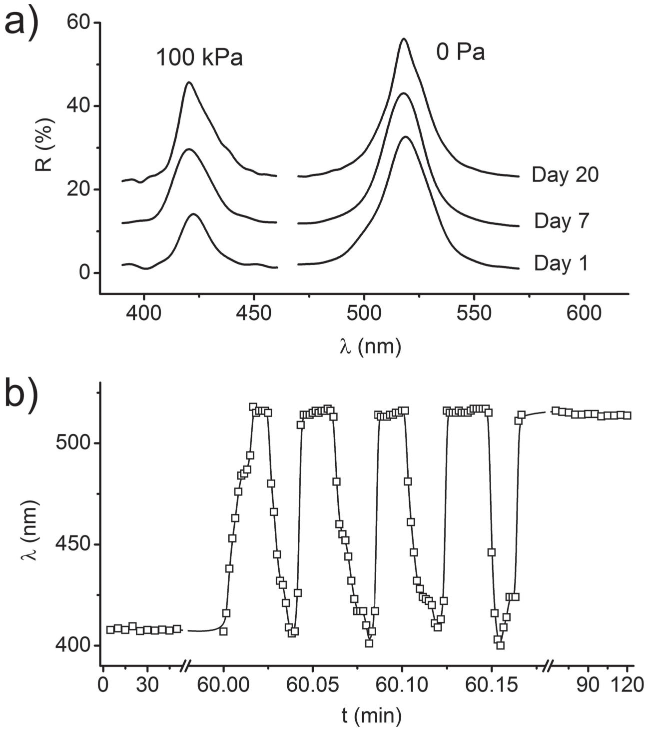

Figure 9. a) Reflection peak-shift by deformation for a same sample at Day 1, Day 7, and Day 20. b) Continuous recording of reflection wavelength where a 1-hour pressing followed by 4 press-release oscillations and then permanent release were applied to the photonic gel.

the fingerprints, which indicate its response time is less than 1 s.[5] In comparison, an opal structure has fast response in both deformation and recovery because the rigidity of opal gel drives it recover in shorter time. A polystyrene colloidal crystal embedded in PEGMA/poly(MOEA) matrix can synchronize with a 10 Hz mechanical oscillation, showing a 50 ms of response time for $\Delta\lambda$ of 40 nm. Although the switching was further pushed to 200 Hz, the reflection intensity in each state could not reach its balanced value.[12] In this work, we developed a PC gel which has simplified synthesis but comparably fast mechanochromic response compared to the above two materials.

Through the encapsulation in polydimethylsiloxane (PDMS), the composite material has good durability for long time storage and fatigue tests. Since the elastic gel has a risk of cracking when the deformation exceeds its critical value, a colorless, transparent and elastic PDMS rubber is used to protect the gel and slow down the evaporation of EG. Tensile test proved that PDMS rubber had better mechanic strength and larger deformation ratio than the photonic gel. (Figure S5) When the photonic gel is encapsulated in PDMS, it presents good adhesion to PDMS rubber, which enables it to be stretched, pressed or bended with corresponding deformation of silicone rubber. The reflection of a photonic gel in PDMS at stress-free (0 Pa) and deformed (100 kPa) state in Day 1, Day 7, and Day 20 proves that it has superior stability for long time storage at room temperature. (**Figure 9**) The composite material also has excellent durability for longtime deformation. In order to prove this, the sample was continuously pressed for 1 hour, then subjected to a press-release oscillation for several cycles, and further kept under stress-free condition for another 1 hour. Except for the first two recovery (whose response time are 1 and 0.2 sec) and first three pressing (whose response time are 0.7, 0.8 and 0.6 s) after longtime deformation, the reflection switching restore to its original speed since the 4th cycle. The superior durability of the composite material lays a solid foundation for its application in mechanical sensors and display screens.

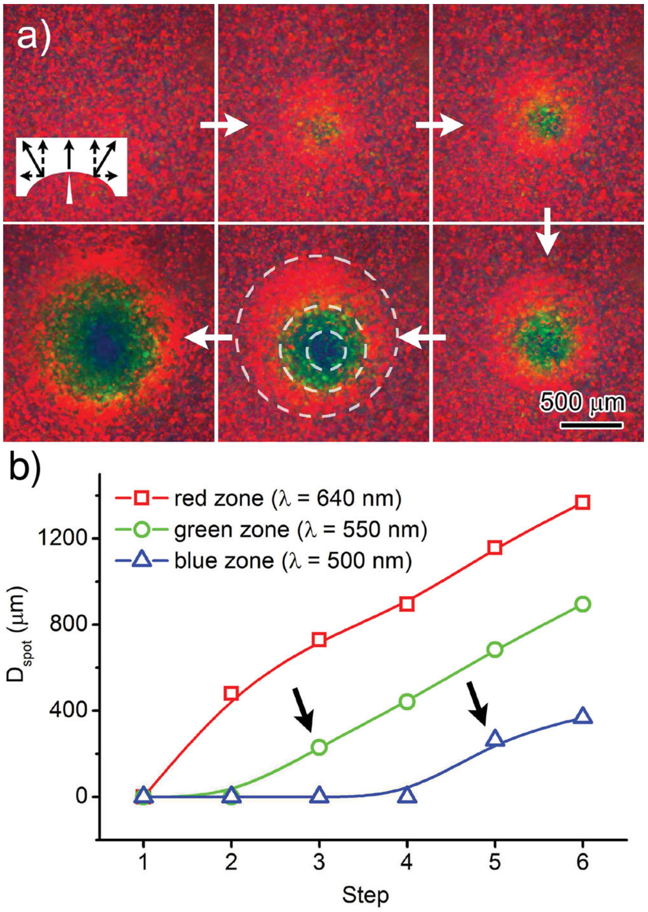

Figure 10. a) A concentric rainbow pattern shows up as the tweezers tip gradually pokes the elastic PC gel. b) Evolution of diameters of red, green and blue region in the process above.

The elastic PC gel encapsulated in PDMS rubber can be used as a soft display panel, on which a gently pressing can produce patterns or pixels with large color contrast. Here, the thickness of bottom PDMS layer for pressing was controlled at 0.5 mm to acquire high resolution and instant response. As shown in **Figure 10**, the gel is composed of many photonic microcrystals, and the bright red color suggests the microcrystals are composed of highly ordered SiO_2 particles. When the tweezers tip poked the composite film and pressed the gel vertically, it caused a color change from red to blue in a circular region, which gradually enlarged as the tip poked deeper. Meanwhile, as the center was vertically pressed by a sharp tip, the annular region around the center would experience partial outward horizontal pressing (Figure 10a inset), which partially neutralized the blue-shift effect in the annular region, leading to a transitional color and concentric rainbow pattern.[3b] For example, in

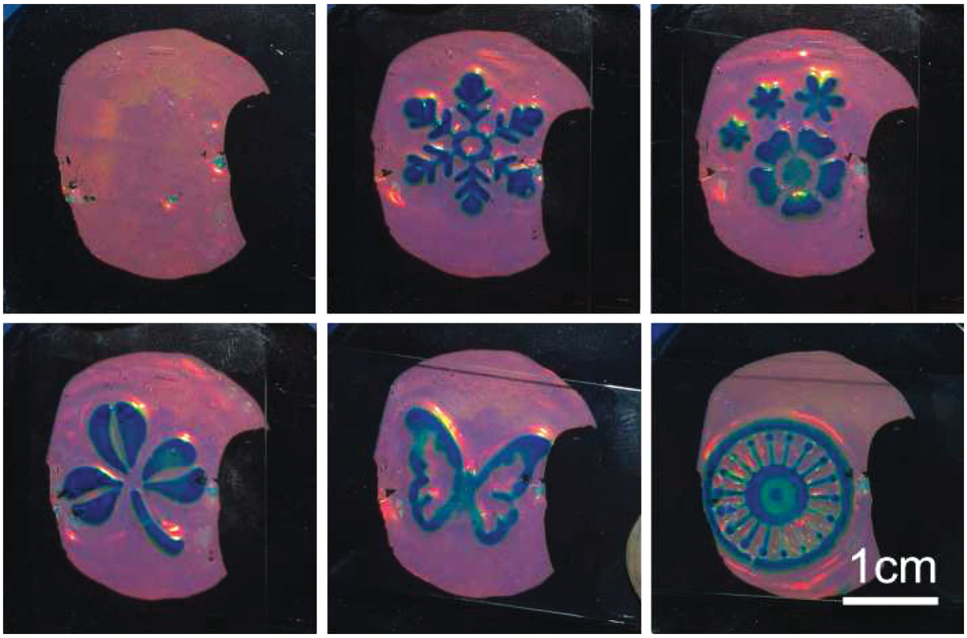

Figure 11. One piece of PC gel can be repeatedly used to show the stamp patterns when it is compressed onto the PDMS rubber.

the 3rd or 4th step in Figure 10a, one can observe a yellow ring between the red circle and green center. The λ of the red, green and blue region are measured to be 640, 550, and 500 nm by reflection spectrometer coupled to the microscope, and the diameters of these color regions in each step indicate that the limited resolution for green and blue spot are 230 and 260 µm respectively. (Figure 10b) It should be noted that this photonic gel has higher resolution when it is not embedded in PDMS. However, the durability will become a big concern in that case. With current achieved resolution, the SiO_2/EG-PEGMA photonic crystal gel in PDMS can topologically show the patterns on stamps without losing any details. (**Figure 11**)

In addition to the monochromatic display of stamp patterns based on topological principals, the controllable display of red, green and blue (RGB) pixels can be realized with simple mechanical operations. As a demonstration, a display panel with 9 pixels was fabricated by encapsulating 9 independent PC gels in PDMS rubber. (**Figure 12**) Instead of a whole piece of PC gel with large area, small but independent PC gels were used to avoid the weakening of mechanochromic effect in a large PC gel. A carbon mask was used to block the unwanted transitional colors in the annular region around the center spot. For each window, a set of coaxially fitted plastic cylinder and hollow cylinder was placed beneath the PC gel. As shown in Figure 12d, the PC gel originally shows green color when no deformation was applied to it. When the plastic cylinder was vertically pushed toward the PC gel, it turns blue immediately due to the gel compression and decreasing of lattice spacing in vertical orientation. The interesting thing is that the gel exposed in the window of carbon mask turns red when the plastic hollow cylinder was pushed toward the PC gel. Because the compression from the annular cross-section of the hollow cylinder leaded to a mass of horizontal pressing pointing to the center of the pixel, which actually cause expansion and increasing of lattice spacing in vertical orientation. Based on this principal, one can manipulate RGB pixels with a same "pushing" operation, and the display is fast and fully reversible. It should be noted that this mode to realize RGB colors is much better than monotonically pressing the original "red" pixel to "green" and "blue one", since the ordered structure will be disturbed and the color fades under large deformation.

3. Conclusions

An efficient synthetic method was developed to prepare mechanochromic SiO_2/EG-PEGMA gel by fixing the metastable SiO_2 CCA in the mixture of EG and PEGMA through photo-polymerization. The solvent wrapped metastable CCA precursor makes it possible to introduce high volume fraction of EG (46 vol%) into the final composite material, which makes it softer and more deformable. Compared to the traditional mechanochromic opal gel, the current material is more sensitive to the external forces and a total 150-nm reflection wavelength shift can be achieved through stretching or bending. At the same time, it retains all the advantages of opal gels, such as fast response in millisecond level (20–200 ms), reversible response, repeatable reflection wavelength and intensity in cycling and fatigue tests. The mechanochromic gel embedded in PDMS was fabricated to be a soft display panel with spot resolution as small as 230 µm in diameter, so that it can topologically show the patterns on stamps. The selective pushing of coaxially fitted cylinder or hollow cylinder pin towards the display screen was utilized to create red, green and blue color pixels, so that the large deformation caused color fading can be avoided. It is believed that the efficient synthetic method and the high-quality mechanochromic photonic gel would promote the application of responsive photonic crystals for potential sensors and display units.

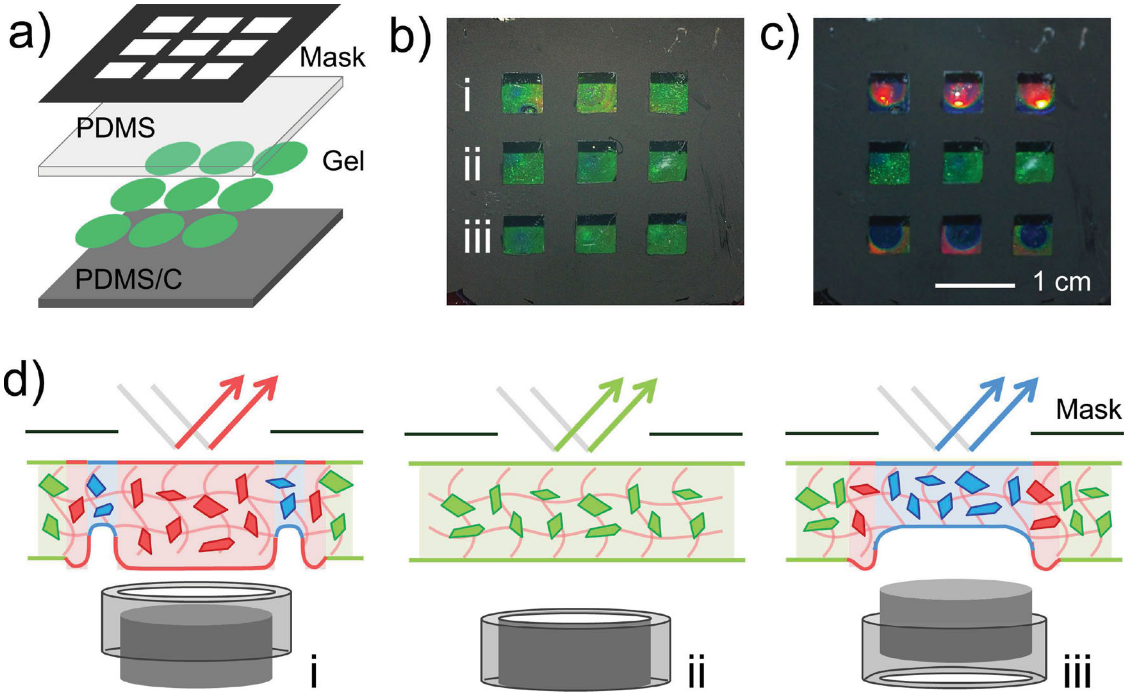

Figure 12. a) Constitution of display screen based on elastic PC gel. b,c) Green pixels turns to blue (3rd row) and red (1st row) d) under the pushing by plastic cylinder and hollow cylinder, respectively.

4. Experimental Section

Materials: Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (28%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Carbon black (99.5%, 30nm) was purchased from Aladdin. Ethylene glycol (EG, 99%) and ethanol (99.9%) were purchased from J&K Co. Ltd. Poly(ethylene glycol) methacrylate (PEGMA, Mn = 360) was purchased from Sigma-Aldrich. Silicone elastomer base and curing agent were obtained from Dow Corning (Sylgard 184). All chemicals were used directly as received without further purification.

Preparation of Mechanochromic Responsive Photonic Crystal Film: Monodisperse SiO_2 particles were first synthesized by Stöber method. The silica particles (0.08 cm^3) dispersed in ethanol (1.0 mL) were mixed with EG (0.077 mL) and PEGMA (0.043 mL). After being evaporated at 90 °C for 2 h and cooled down to room temperature, the mixture was concentrated to a liquid suspension (0.2 mL) with pale iridescent color. The designed volume fraction of SiO_2 particles in the suspension would be 40%. Part of the liquid suspension (0.03 mL) was sandwiched between two glass slides separated by an interval (~0.18 mm) and placed without disturbance for 10 min to form a metastable CCA precursor. After being exposed to UV light (365 nm, 4.8 mW/cm^2) for 20 min, the liquid precursor was polymerized to form elastic photonic crystal gel.

Encapsulation in PDMS Rubber: The as-prepared PC gel was sandwiched between a transparent and colorless PDMS top layer and a PDMS-carbon bottom layer containing carbon nanoparticles. First, the silicone elastomer prepolymer, curing agent and carbon powders were mixed in a mass ratio of 20:2:1 by mechanical stirring. The above mixture (8 mL) was transferred to a clean Petri dish with diameter of 47 mm, and cured at 60 °C for 2 h to produce a PDMS-C film with specific thickness. After the elastic photonic gel was placed on top of the PDMS-C layer, mixture of elastomer prepolymer and curing agent (10:1) was poured to cover the gel completely. The top PDMS layer was cured at room temperature overnight to seal the photonic gel inside PDMS matrix in the end.

Characterization: The particle size was determined by a JEOL JEM-2100 transmission electron microscope. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in dark-field mode. The reflection spectra were measured by an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection/back scattering probe, where both the incident and reflective angle were fixed at 0°. The external force was detected by a HP-50 force gauge.

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