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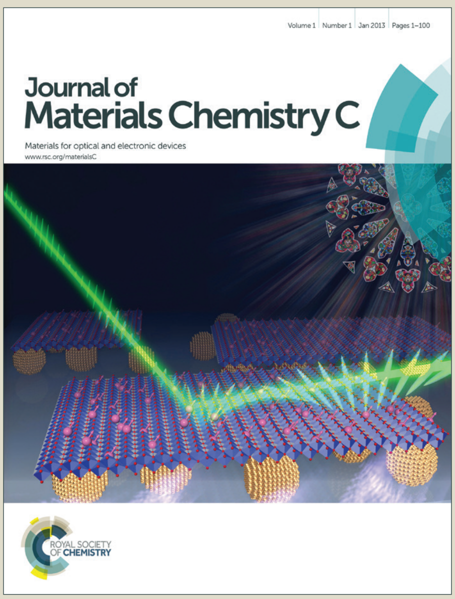

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Soaking Based Invisible Photonic Prints with Fast Response and High Resolution

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A soaking based invisible photonic print is prepared by regionally selective hydrophobization of SiO_2/PEGMA photonic paper under mask. The patterns on the prints are invisible at dry state but seenable in water, because a nonuniform swelling behavior of the hydrophilic and hydrophobic regions of the paper induces a different lattice expansion and a large color contrast between the pattern and the background. Due to the uncrosslinked characteristic and superior swelling ability of current photonic paper, the invisible patterns printed on it can be reversibly shown and hidden in several seconds and its resolution reaches the micrometer scale, both of which will favor its application in antifraud label or identification recognition in our daily life.

1. Introduction

Responsive photonic crystal (RPC) is one kind of smart materials whose optical properties can be tuned by physical or chemical means, such as heat[1], pressure[2, 3], humidity[4-8], light[9], electric[10] and magnetic field[11-13] etc. It has aroused great enthusiasm in the field of chemistry and material science since the RPCs can be potentially used in color displays[14, 15], biological[16-18] and chemical[19, 20] sensors, coatings and printings[21-23], photocatalysts[24, 25] and solar cells[26, 27]. Among all these applications, the revealable invisible photonic prints for antifraud purposes [3, 28] are extraordinarily useful in our daily life. For instance, an invisible pattern shown by water soakage is printed on a magnetically assembled $Fe_3O_4@SiO_2$/(PEGDA-PEGMA-TPM) photonic crystal (PC) paper based on the control of crosslinking level and swelling ability between the pattern and background[29]. The crosslinking won't change the refractive index or lattice constant too much so that the original contrast of reflection wavelength ($\Delta\lambda_0$) is hard to be aware of. When the prints are dipped in water for several minutes, a large contrast of reflection wavelength ($\Delta\lambda_t$) appears due to the different swelling speed and lattice expansion of the pattern and the background. Another successful example of invisible photonic print is prepared on magnetochromic (Fe_3O_4@C-EG)/PDMS rubber, where the hidden pattern can be revealed by the exertion of magnetic field.[30] The pattern is invisible under normal condition because the pattern and background contain EG droplets of magnetic particles and dried cavities with residual particles respectively, and both of them show the same intrinsic color of magnetite. When the magnetic field is applied, the pattern shows specific structural color due to magnetic assembly while the background keeps unchanged, which reveals the pattern instantly. Furthermore, invisible prints shown by deformation has also been demonstrated on a mechanochromic photonic paper [31, 32]. The pattern is printed based on the control of deformation ability through chemical crosslinking, so that the pattern and background have non-uniform mechanochromic response to external stimuli. Since the crosslinking causes slight change in reflection wavelength, the pattern is hidden in relaxed condition. As the elastic photonic paper is stretched or squeezed, the crosslinked and uncrosslinked region will deform differently, which leads to a large contrast of reflection wavelength and the reveal of invisible pattern.

Recently, our group has demonstrated the first case of invisible photonic prints shown by water soaking. However, the showing speed and the resolution of patterns are not satisfactory due to the relatively slow swelling of photonic paper and low density of photonic structures within it. In that case, the reflection of the pattern which retains the structure of original PC paper usually red shifts during swelling. While the reflection of the background, which is further crosslinked through the formation of Si-O network, slightly red shifts. Therefore, the contrast of reflection wavelength reveals the pattern eventually. Since the wavelength shift of original PC paper is dominant for the showing of patterns, its swelling ability and swelling speed will determine the performance of invisible prints. For $Fe_3O_4@SiO_2$/(PEGDA-PEGMA-TPM) photonic paper used in previous work, high crosslinking is necessary to fix the dynamically changed magnetic assembled photonic structure, because the volume fraction of particles in precursor is only about 0.0015 and no enhancement of solidification from inorganic particles can be utilized. Therefore, the chemically crosslinked structure results in a relatively slow

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swelling speed of polymer matrix. It usually takes several minutes to show the pattern with a 90-nm contrast of $\Delta\lambda$. The slow swelling will then amplify the prints' thickness and decrease the resolution especially for those micro patterns, because the surface crosslinking can't restrict the swelling inside the polymer matrix, and the color change may happen right under the crosslinked surface if the swelling process is adequately long. Therefore, new photonic paper with enhanced swelling abilities is desired for fabricating invisible prints with fast revealing speed and high resolution.

In this work, a hydrophilic photonic crystal film was prepared by fixing the metastable SiO_2 colloidal crystals in PEGMA through photo polymerization. The SiO_2 particles with high volume fraction have strong interactions with PEGMA, so that a solid polymeric film can be formed even without the addition of chemical crosslinker. Due to the uncrosslinked characteristic, the photonic paper has superior swelling ability, which leads to a large lattice expansion and reflection wavelength redshift (150 nm) in several seconds. Using this PC film as paper, we have fabricated an improved soaking based invisible photonic print through regionally selective hydrophobization of photonic paper under mask. Within 10 seconds, the as-prepared invisible photonic patterns with resolution up to 100 micrometers can be reversibly shown by water soaking and hidden by drying in air.

2. Experimental

2.1 Chemicals

Tetraethylorthosilicate (TEOS, 98%) and ammonium hydroxide solution (28%) were purchased from Sinopharm Chemical Reagent Co. Poly (ethylene glycol) methacrylate (PEGMA, Mn = 360) and ethoxylated trimethylolpropane triacrylate (ETPTA, Mn = 428) were purchased from Sigma-Aldrich. Ethanol (99.9%) was purchased from J&K. Trichloro (1H,1H,2H,2H-perfluorooctyl) silane (97.0%) and 2-Hydroxy-2-methylpropiophenone (DMPA, 99%) were purchased from TCI Co. Ltd. Commercial optical adhesive NOA 61 was purchased from Norland.

2.2 Preparation of photonic crystal paper

SiO_2 particles prepared by Stöber process with approximately diameter of 180 nm were dispersed in ethanol and then mixed with acrylate monomer (PEGMA or a mixture of PEGMA and ETPTA) and photo-initiator (DMPA, 5 vt %). The total volume of the mixture was fixed at 1.2 mL, which contained 40 μL of silica, 60 μL of acrylate monomer and about 1.1 mL of ethanol. The solution containing silica particles was homogenized by vortex mixing and sonication, and then transferred to an oven at 90 °C. After 2-hour evaporation of ethanol in oven, the solution was concentrated to 100-μL precursor. Typically, 30 μL of precursor solution was sandwiched between a glass slide and a piece of hydrophobic cover glass. The photonic crystal film with reflection peak at about 470 nm was obtained once the liquid precursor was exposed to UV light (365 nm, 4.8 mW/cm^2) for 1 min. Finally, the photonic crystal film was fixed on the glass slides or transparency by NOA61 to produce a piece of photonic paper for the following printing.

2.3 Printing invisible pattern on photonic crystal paper

First of all, 3 μL of trichloro(1H,1H,2H,2H-perfluorooctyl) silane was added to a glass vial placed in a desiccator. The photonic crystal paper protected by a steel grid or a parafilm mask was then placed on top of the vial. The desiccator was vacuumed for 30 minutes to complete the surface modification. Finally, the mask was removed and the invisible photonic pattern was obtained. Generally, the protection from parafilm is very effective and no fluorosilane vapor will diffuse into the protected PC film, while the protection from steel grid is affected by the surface flatness and the contact between the grid and PC film. In experiment, the steal grid and the PC film is fixed by binder clips to avoid the diffusion of fluorosilane vapor as much as possible.

2.4 Characterization

The assembly of silica particles within the photonic crystals film was observed by a Phenom G2 Pro scanning electron microscope. The optical microscope images were taken by 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 °. In order to record the evolution of reflection signal during the water soaking and drying process, the reflection spectra were continuously recorded by spectrometer in the step of 1 sec.

3. Results and Discussions

3.1 Fabrication and Working Mechanism of Invisible Photonic Prints

Typically, the fabrication of invisible photonic prints includes the preparation of photonic crystal paper and the printing of invisible patterns. (Figure 1) First of all, a hydrophilic PC film was prepared by fixing the metastable SiO_2 crystalline colloidal arrays (CCAs)[33] in the matrix of PEGMA without chemical crosslinking through photo-polymerization. The PC film contains SiO_2 particles with a total volume fraction of 0.3, and 60% of these particles are assembled into colloidal microcrystals while rest of them are randomly stacked in the film. The PC film was fixed on the glass slide or transparency by optical adhesive (NOA61). A parafilm or metal mask with desired patterns was then tightly attached to the PC film to protect part of the hydrophilic surface from the following surface modification. When the PC film was placed in the environment filled with fluoroalkylsilane vapor, the exposed part would lose their swelling ability due to the surface hydrophobization while the shielded part would not. After removing the mask, an invisible photonic print with different swelling ability in the region of pattern and background was finally obtained.

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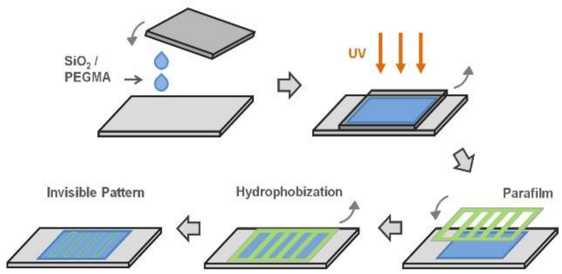

Fig.1 Schematic illustration to the fabrication of soaking based invisible photonic prints.

The working mechanism of soaking based invisible photonic prints is explained in Figure 2. Generally, the pattern is invisible at dry state because the surface hydrophobization neither changes the photonic structure nor leads to any color contrast between pattern and background. Once the paper is soaked in water, it selectively diffuses into the paper from the hydrophilic window, which leads to polymer swelling, expansion of crystal lattice, redshift of reflection and change of structural color from blue to red. Meanwhile, the color of hydrophobic region scarcely changes, which forms a large color contrast with the hydrophilic region and reveals the invisible pattern. After the evaporation of absorbed water, the swelled photonic composite recovers to its original state, so that the small color contrast will hide the pattern again. As a simple demonstration, five stripes are printed on the blue photonic paper as invisible pattern. They show five red stripes as soon as the paper is soaked in water for 10 seconds. After wiping up the water on the surface, the red stripes will disappear in several seconds and the whole showing-hiding process is fully reversible.

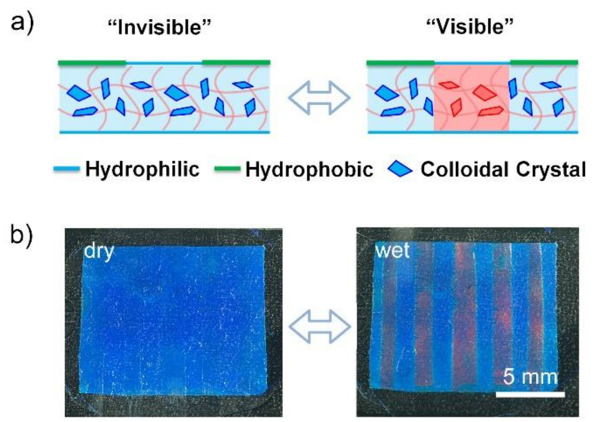

Fig.2 a) Mechanism of invisible photonic prints shown by water soakage. b) Five stripes are hidden in dry state and shown in wet state.

3.2 Hydrophilic Photonic Paper with No Crosslinking

The fast showing and hiding of invisible photonic prints originates from a highly hydrophilic photonic paper with completely no chemical crosslinking of polymer matrix. Different from the Fe_3O_4@SiO_2/(PEGDA-PEGMA-TPM) photonic paper used in our previous work, the current SiO_2 colloidal microcrystals can be fixed in pure PEGMA without addition of any crosslinker, because the inorganic particles with high volume fraction have adequately strong interactions with PEGMA, which facilitates the formation of a solid polymeric film. Due to the absence of crosslinker, the PEGMA matrix will swell more and faster in water, which leads to a quicker change and larger shift of reflection wavelength for unmodified photonic paper. In order to confirm the dense packing of particles, a blue SiO_2/PEGMA photonic paper fixed on a transparency is investigated. (Figure 3a) In its optical microscope image, dense blue microcrystals with diameter of 70~90 μm and transparent intervals can be observed, which correspond to SiO_2 colloidal crystals and random stacking of SiO_2 particles respectively. (Figure 3b) The SEM images of SiO_2 microcrystals show a highly ordered arrangement of SiO_2 particles, which is consistent with the strong and monochromic reflection behavior. (Figure 3c, 3d). At the same time, the amorphous region composed of randomly packed silica particles is transparent due to the matching of refractive index between SiO_2 and PEGMA, so that the structural color of colloidal microcrystals won't be disturbed by the scattering of disorderly particle stacks. In a word, the high volume fraction of particles helps to the production of SiO_2/PEGMA photonic paper with no chemical crosslinking, which leads to a quick color change and large color contrast during the showing of invisible patterns.

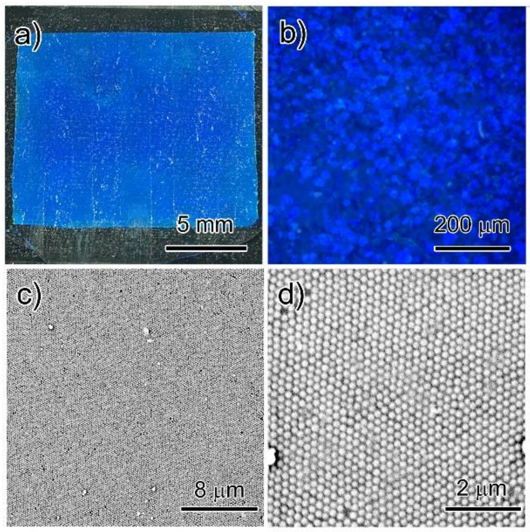

Fig.3 a) Digital photo, b) microscope image and c-d) SEM image of SiO_2 colloidal microcrystals inside a SiO_2/ PEGMA photonic paper.

In order to prove the superior swelling ability of the uncrosslinked SiO_2/PEGMA paper, the evolution of reflection signal during the swelling process is investigated to evaluate the responding speed. (Figure 4a) As the PC paper being soaked in water, the reflection spectra are continuously recorded in the following 1 minute, which are converted into a

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contour map with time (t) in x-axis, reflection wavelength (λ) in y-axis and reflection intensity (R) in color for further study. Generally, the reflection wavelength change (Δλ) can be tracked from the trend of "reflection bands" in the contour map, while the change of reflection intensity (ΔR) can be characterized by the band colors.

In the beginning, there is only one horizontal band at 469 nm with intensity above 40%, which corresponds to the blue color of the dried photonic paper. Once the paper is soaked in water, the original reflection band instantly splits into a higher and a lower band, which represents the evolution of reflection of surface and inner layer, respectively. The higher band at 618 nm appears as soon as the water contacts the paper, leading to a large Δλ comparing to the original reflection. In the following 1 min, the reflection wavelength of surface layer slightly increases to 624 nm and its density continuously increases, which suggest the swelling of paper surface is thorough and extremely fast. Meanwhile, the lower band quickly disappears in 10 seconds, which suggests the water diffuses into the inner layer and swells all the photonic crystal film in very short time. According to the trends of higher and lower band, it can be concluded that the swelling speed is much faster than the diffusion speed for the uncrosslinked SiO_2/PEGMA paper. As shown in Figure 4b, the film turned to red in 10-20 seconds and its structural color became intense in the following seconds. Both the dynamic reflection spectrum and the observation of color change prove that the uncrosslinked paper has a short response time (~ 10 sec) and a large color contrast (Δλ = 150 nm) between dry and wet state.

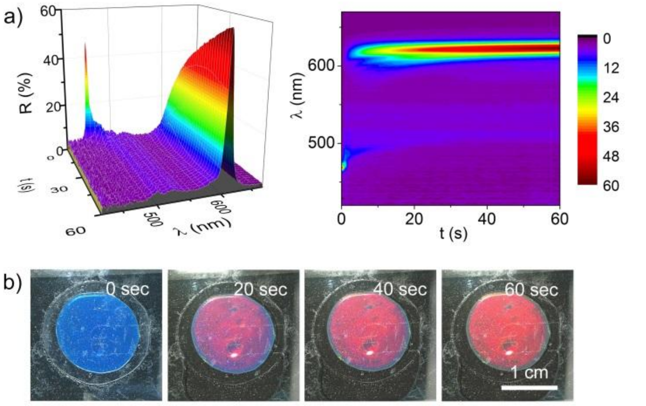

Fig.4 a) 3D surface map and color-filled contour map show the evolution of reflection signals for uncrosslinked SiO_2/PEGMA photonic paper when soaked in water. b) Photonic paper changes color accordingly during the swelling process.

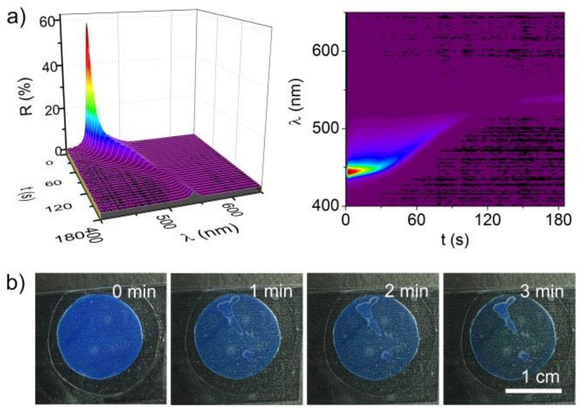

Fig.5 a) 3D surface map and color-filled contour map show the evolution of reflection signals for crosslinked SiO_2/PEGMA/ETPTA photonic paper when soaked in water. b) Photonic paper changes color accordingly during the swelling process.

Based on the aforementioned discussion of crosslink level and responding speed, one can imagine that the introduction of crosslinking will inhibit the swelling, which is apparently unfavorable to the working of invisible photonic prints. Here, a crosslinked PC paper composed of monomer PEGMA (80 %) and crosslinker ETPTA (20 %) is used as a counterexample of the uncrosslinked paper. (Figure 5) Once the paper is soaked in water, the reflection band slowly rises from 440 to 538 nm in 3 min with a disconnection in the middle. There is only 35-nm of reflection wavelength change in the first 1 min, which is much smaller than that of the uncrosslinked paper (150nm). The intensity first decreases then increases due to the match of refractive index. After 3 min, the reflection intensity has not been recovered yet. While for the uncrosslinked paper, the intensity even increases after 1 min. Both the change of reflection wavelength and intensity prove that the swelling is much slower for a crosslinked photonic paper. In observation by naked eye, the blue photonic paper does not change color but gradually turns transparent in 3 min, which is consistent with the evolution of reflection signals. Based on working mechanism of invisible photonic prints, the small change of structural colors will be unfavorable to the showing of invisible patterns. Therefore, a highly hydrophilic photonic paper with good swelling capability is essential to the fabrication of fast responsive invisible photonic prints.

In addition, the structural color of SiO_2/PEGMA photonic paper is slightly affected by the incident and viewing angle, which makes it suitable for fabrication of wide-angle prints. As shown in Figure 6, the reflection spectra of dry and wet photonic paper are recorded with incident angle changing from -23° to 23°. The reflection of the dry paper blue shifts from 435 nm to 427 nm as the incident angle increased from 0° to 23°, while that of the wet paper blue shifts from 601 nm to 585 nm accordingly, which suggest the structural color of current photonic paper is scarcely changed in a specific range of viewing angles no matter the paper is dry or wet. The little influence of angle upon the structural color not only guarantees the showing effect of invisible photonic prints from wide viewing angle but also makes it possible to realize the

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invisible prints on a curved or flexible substrate, such as a glass vessel, which is favorable to the practical usage.

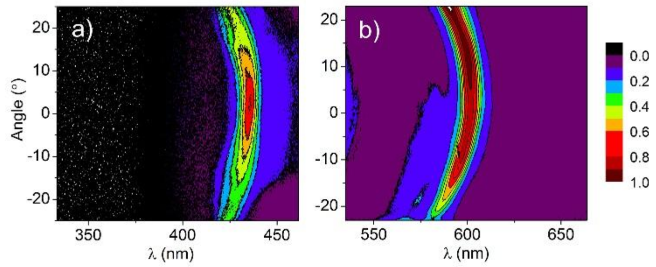

Fig.6 Angle-dependent reflection spectra of SiO_2/PEGMA photonic paper at a) dry and b) wet state.

3.3 Invisible Photonic Prints with Fast Response and High Resolution

The superior swelling ability of uncrosslinked photonic paper renders fast showing of invisible patterns. Using the uncrosslinked and hydrophilic SiO_2/PEGMA photonic crystal composite as paper, one can print invisible patterns on it through hydrophobic modification on selected region of the paper, and the patterns can be quickly and clearly revealed by water soakage. As shown in Figure 7a, the original reflection of the hydrophilic (469 nm) and hydrophobic (468 nm) region are very close since the surface hydrophobization doesn't change the photonic structure of the paper. Their structural colors are close either, so that the pattern is invisible when the paper is dry. When the hydrophilic region is soaked in water, the original reflection rapidly decreases and a new reflection at 618 nm quickly rises, whose intensity reaches 57% of the original one in 10 seconds. The hydrophilic region may be purple in the first several seconds due to the mixing of blue and red color, but eventually it turns pure red in very short time. On the other hand, when the hydrophobic region is soaked in water, only a weak reflection at 585 nm appears due to the poor surface swelling caused by hydrophobic modification. The intensity of the new reflection is so weak that the structural color of the hydrophobic region remains blue. Due to the unequal response of hydrophilic and hydrophobic region on photonic paper, a large color contrast is created between them, which reveals the invisible pattern.

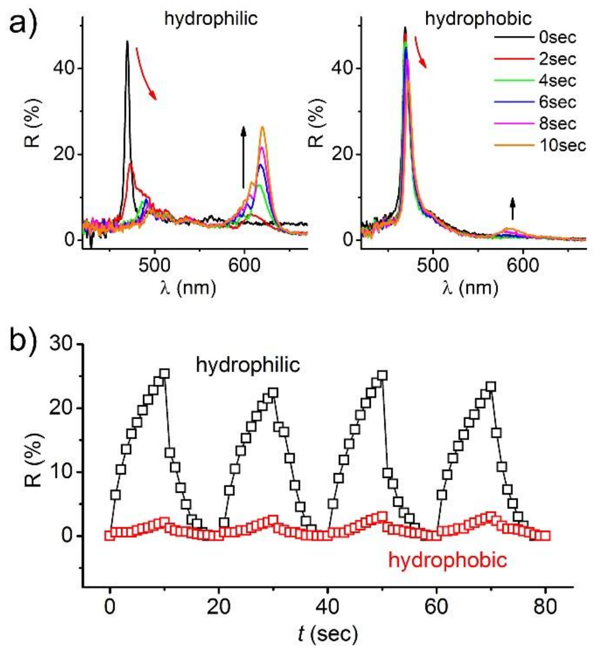

Fig.7 a) Evolution of reflection spectrum of hydrophilic and hydrophobic region after being soaked in water for 10 seconds. b) Intensity change of the emerging peak in 4 continuous soaking and drying process.

The showing and hiding of the invisible photonic pattern is reversible in practical usage. According to the discussions above, the color contrast between the hydrophilic and hydrophobic region is majorly caused by the difference in intensity of the emerging reflection at 618 and 585 nm. Therefore, the showing and hiding of photonic patterns can be characterized through the intensity changes of these two reflection peaks. Typically, in 10 seconds of water soaking, the intensity of the hydrophilic region rises rapidly from 0 to 25%, while that of the hydrophobic region slightly increases from 0 to 3%, which leads to a large color contrast and reveals the pattern in very short time. In the next 10 seconds of drying, the reflection intensity of both the hydrophilic and hydrophobic region decreases to 0, so that the color contrast disappears and the pattern recovers to invisible state. (Figure 7b) In the 4 continuous cycles of soaking and drying processes, the reflection intensity of hydrophilic and hydrophobic region separate and merge periodically, which proves that the showing and hiding of invisible patterns can be repeated for many times. In practical usage, the invisible photonic prints can be stored for months, and it works well for at least 20 recycles or even more. Here, we show the hiding and showing of invisible photonic prints in the first 6 cycles. (Figure 8) It will eventually lose effect when all the hydrophobic molecules are washed down by repeated soaking in water.

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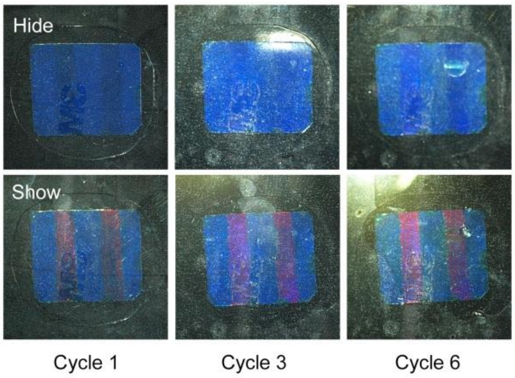

Fig.8 Reversible showing and hiding of invisible photonic prints in the 1st, 3rd and 6th round of continuous soaking and drying process.

In addition to the fast response in showing or hiding, the superior swelling ability of uncrosslinked photonic paper also renders the prints a high resolution in the showing of invisible patterns. It should be noted that the printing of invisible patterns are realized by selective surface hydrophobization, which does not change the inner hydrophilic characteristics of photonic paper. At the beginning of water soakage to show the invisible patterns, the swelling of photonic paper and the change of structural colors are restricted within the hydrophilic window, so that the revealed patterns are exactly the same as the distribution of hydrophilic and hydrophobic regions. (Figure 9a) However, as the soaking proceeds, the infiltrated water molecules will diffuse in all directions in the inner layer. The surface hydrophobization can't restrict the diffusing of water molecules inside the photonic paper, so that the swelling will gradually occur right beneath the hydrophobic surface layer. Therefore, the revealed invisible pattern seems to be "amplified" after long time of swelling, which decreases the resolution of the patterns. Apparently, such negative influence upon the resolution can be addressed by using an extremely hydrophilic photonic paper whose swelling speed is larger than that of diffusion. Only in that case, the patterns will retain the high resolution of masks, because a sufficiently large color contrast ($\Delta\lambda$) can form in very short time before the swelling exceeds the restriction of surface modification. Fortunately, the current SiO_2/PEGMA photonic paper qualified for the requirements, so that high resolution can be realized.

The dependence of high resolution upon the good swelling abilities can be proved by the showing of an invisible straight line with width of 400 μm. (Figure 9b) The hydrophilic straight line printed on a blue photonic paper is invisible at dry state, which quickly turns to red with sharp boundary after the photonic paper is soaked in water for 10 seconds. There are microcrystals with red, green and blue colors within the line at the same time, which are caused by the gradual lattice expansion of photonic crystals along the direction of water diffusion. As the soaking proceeds to 3 min, the fully swelled line turns to pure red while the hydrophobic background becomes green because the swelling has expanded to the hydrophobic region beside the line. It makes the boundary hard to be distinguished and the straight line much broader. The microscopic analysis proves again that the showing of high resolution patterns can only be realized in the beginning of the swelling, which requires a large color change to be achieved in the same short time.

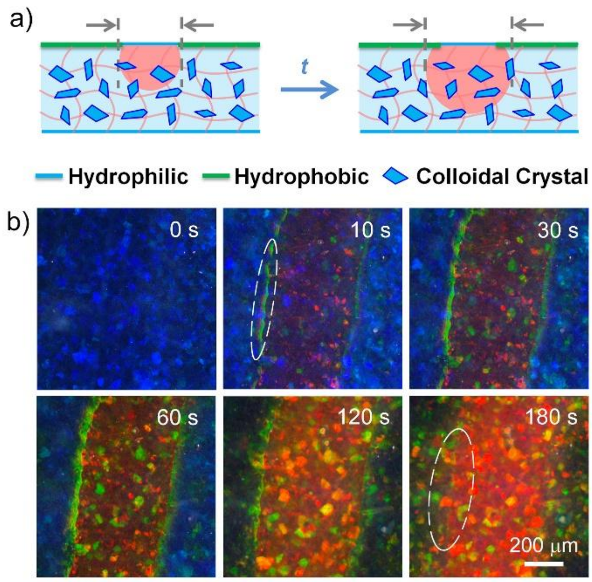

Fig.9 a) Schematic illustration to the expansion of invisible pattern after long-time swelling. b) Microscope observation of showing of an invisible line by water soaking.

As a demonstration to the fast revealed and high resolution invisible photonic prints, a straight line and a circular array in micro scales have been printed on the current SiO_2/PEGMA photonic paper. First of all, the straight line with width of 120 μm is printed using parafilm mask to protect most of the hydrophilic paper from surface hydrophobization, followed by the removal of parafilm mask after modification. (Figure 10a, b) The hydrophobic blue line is basically invisible at dry state, but it can be revealed as the background turns red and the straight line maintains blue after the paper is soaked in water for several seconds. In addition to parafilm, a metal frame like a 30-mesh stainless steel grid can also be used as protective mask during surface hydrophobization process, which leads to a hydrophobic circular array printed on the hydrophilic photonic paper. (Figure 10c, d) Once the print is soaked in water, the circular array can be seen as the background changes from blue to red due to swelling induced lattice expansion. Based on the current SiO_2/PEGMA photonic paper, the resolution of invisible photonic prints can easily reaches about 120 μm, which may get better with the introduction of more sophisticated masks.

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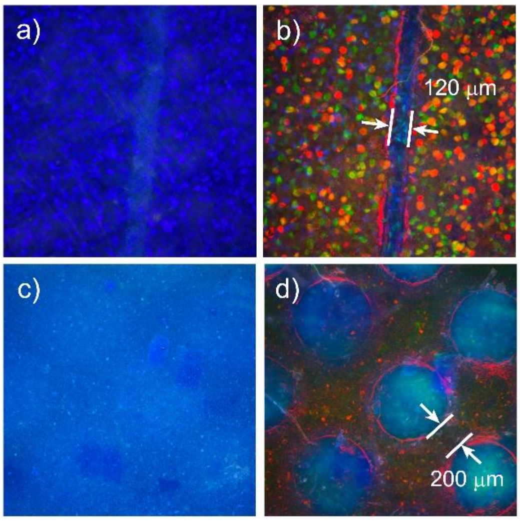

Fig.10 Invisible photonic prints of a, b) a single line and c, d) an orthogonally arranged circular array shown by water soaking.

4. Conclusion

In summary, a highly hydrophilic photonic crystal film was prepared by fixing the metastable SiO_2 colloidal crystals in the polymeric matrix of PEGMA through photo polymerization. Using this film as paper, we have fabricated a soaking based invisible photonic print through regionally selective hydrophobization of paper under mask. The invisible patterns can be revealed by water soakage because a nonuniform swelling behavior of hydrophilic and hydrophobic part of paper induces a different lattice expansion and a large color contrast between the pattern and the background. This pattern can also be hidden after being dried in air, and the showing/hiding is fully reversible. Compared to the original soaking based invisible photonic patterns printed on Fe_3O_4@SiO_2/(PEGDA-PEGMA-TPM) paper, the current sample has much faster response and higher resolution, which can be attributed to the using of this new uncrosslinked SiO_2/PEGMA photonic paper. Its superior swelling ability makes it possible to show an invisible photonic pattern with resolution up to 100 micrometers by several seconds of water soakage. It is believed that with these merits, the soaking based invisible photonic prints will find its applications in antifraud label, identification recognition and dynamic signage.

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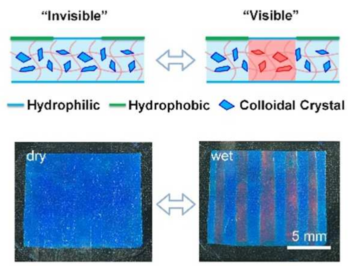

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