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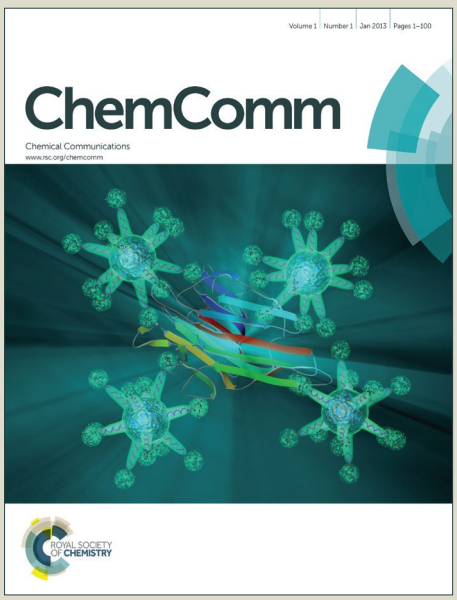

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Old Relief Printing Applied to Current Preparation of Multi-Color and High Resolution Colloidal Photonic Crystal Patterns

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Monodisperse SiO_2 colloids are assembled into colloidal crystals in the mixture of monomer and solvent, which is transformed into mechanochromic photonic crystal paper by polymerization. Follow the relief printing strategy, the printing plates are pressed to the paper to generate letters or images due to the contrast of structural color between deformed and undeformed paper, and the images can be permanently retained through UV curing. The wide tuning range in structural color for the current paper under deformation helps to realize multi-color printing. The localized deformation among or even inside the colloidal microcrystals renders the paper precise mechanochromic response to the printing plates and leads to the production of high resolution photonic crystal patterns.

Relief printing is an old printing method, which applies ink to the raised surface of letters or patterns and then achieves images by pressing the paper to the inked printing plate. It was first invented by Chinese (Sheng Bi) in form of letterpress printing with movable ceramic type in 1040 AD, and was developed into a modern industrial process by German (Johannes Gutenberg) 400 hundred years later. Compared to regular printing with contrast between ink marks and white paper, "photonic printing" can be understood as a process to create contrast of structural color between two different photonic structures. It has attracted broad interests in interdisciplinary field of chemistry, physics and material science since the discovery of photonic crystal in 1987[1, 2], because it is a fundamental technique to realize the application of photonic crystals in sensing[3-9], optical tuning[10-13], antifraud identification[14-18], photocatalysis[19, 20], solar cell[21-23] and photonic circuits. We are curious about whether the old relief printing can be utilized to fabricate high resolution photonic prints for current applications.

Except for the ink-jet printing[24, 25], most reported photonic printing techniques are based on the change of photonic structures in selected region of a premade photonic crystal film. In principle, any structural factors, including the refractive index, lattice constant and crystal orientation, can be tuned spatially to form different structural colors between pattern and background.[26-29] In practical operation, the printing process usually integrates polymer swelling, magnetic tuning or photo polymerization, etc. For example, when the PS-PMOEA photonic paper is swollen by polymerizable monomer and irradiated by UV light under a photo mask, the pattern of the mask will be printed onto the paper. Because the expanded photonic structures in the exposed region are fixed while the shielded region recovers its original color after rinsing and drying, which forms a large contrast in color between them and produces a permanent pattern.[28] In addition, with magnetically responsive colloidal dispersion as ink, one can prepare photonic patterns through repeated magnetic alignment, orientational tuning and photo polymerization following typical photolithographic procedures. Two fixed one-dimensional photonic structures with distinctive orientations also produces a contrast in color when the incident light and observation angle are kept the same.[30] Overall, most printing are developed based on swelling induced lattice expansion, and rare efforts have been paid to the using of mechanochromic photonic paper.

In this work, we show that the old relief printing strategy can be used to prepare multi-color and high resolution patterns on mechanochromic SiO_2/EG-PEGMA photonic crystal paper. Due to the sensitive mechanochromic response, the photonic paper will instantly show the patterns once the printing plate or stamps are pressed on it, and the photonic patterns can be permanently fixed by a fast UV curing process. Multi-color printing can be expected as the structural color can be controlled by the degree of deformation. High resolution printing can also be achieved since the superior mechanochromic photonic paper can respond to localized deformation within very small range.

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Typically, the fabrication of high resolution photonic crystal patterns includes the preparation of mechanochromic photonic paper, the relief printing with premade stamps and the permanent fixing of photonic crystal patterns. (Fig 1a) First of all, the gel like photonic paper is prepared by fixing the metastable SiO_2 colloidal microcrystals in the matrix of ethylene glycol (EG) and poly(ethylene glycol) methacrylate (PEGMA) through photo-polymerization.[31] The photonic paper is swelled with the mixture of EG and poly(ethylene glycol) diacrylate (PEGDA), producing a mechanochromic but curable photonic material. When the photonic paper is pressed by printing plate, one can immediately observe a colourful pattern due to the nonuniform deformation and color change of photonic crystal in different regions of the paper. Then, the photonic paper swelled by crosslinker is irradiated by UV light, so that the color contrast and the photonic patterns can be permanently retained.

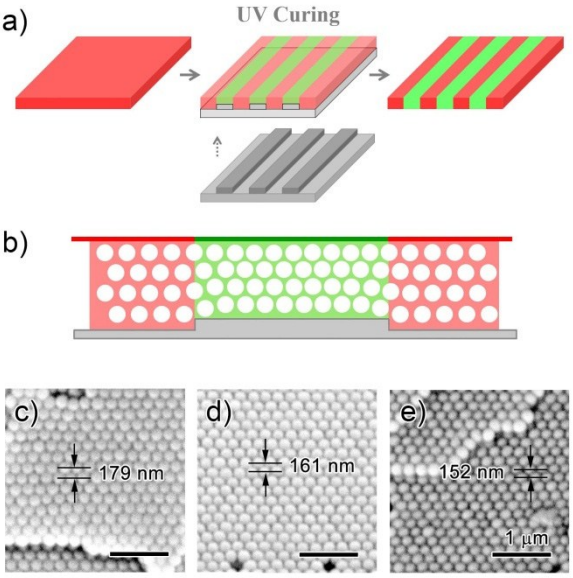

Fig 1. a) Printing patterns through pressing printing plate on mechanochromic photonic paper, UV curing and removal of printing plate. b) Scheme to the deformation induced change of structural color. Cross-section SEM images of PC film when it turns from c) red to d) green and e) blue.

The mechanochromic response and fast curable characteristic of photonic paper are two keys to the successful printing of photonic patterns. According to our previous research works, the SiO_2/EG-PEGMA photonic crystal film has superior mechanochromic response due to its gel-like constituent and deformable structures. The structural color of the paper changes by deformation due to the corresponding change of lattice constant, while it recovers to the original color once the pressing, stretching or squeezing are withdrawn. Such mechanochromic properties are kept even after the introduction of chemical crosslinker, which renders the photonic paper extra curable characteristic. Typically, when the red photonic paper is pressed by stamps, the raised parts of the stamp press the paper locally, so that the structural color of the deformed part changes from red to green due to the compression of crystal lattice. (Fig 1b) Meanwhile, the rest part of the paper keeps its original color as no deformation is applied. As a result, a distinct color contrast between these two parts is produced due to the nonuniform deformation which transfers the exact pattern on stamp to the photonic paper. The shrinkage of crystal lattice can be proved by the cross-section SEM image of the original and the deformed PC film.(Fig 1c-1e) For the convenience of understanding, colloidal microcrystals with (111) face as the exposed facet are selected for comparison, and their SEM images show that the lattice spacing does decrease from 179 nm (red PC, λ = 622 nm) to 161 nm (green PC, λ = 565 nm) and even 152 nm (blue PC, λ = 492 nm). These lattice constants are smaller than the values calculated from the reflection wavelength because the evaporation of EG in sample preparation for SEM measurement will decrease the lattice spacing.

It is worth mentioning that the flexible use of EG plays an important role in the whole printing process. Based on the mechanism of photonic printing, the deformation induced color change and the fast crosslinking under UV irradiation are crucial to the success of printing. For the aspect of mechanochromic response, the introduction of high volume fraction of EG has been proved to be the reason for the formation of more deformable photonic composite than most reported opal gels, which renders it improved mechanochromic sensitivity to weak external force, extended color tuning range from red to blue as well as fast and reversible response in millisecond level.[32] As for the fast curing of photonic composites, the mixing of EG with crosslinker greatly helps the infiltration of PEGDA into the photonic paper. Pure PEGDA will extract EG from the photonic paper rather than infiltrate into the paper, which leads to the dimming of photonic paper. However, when the PEGDA is mixed with EG in a ratio of 1:1, it can infiltrate into the photonic paper more easily and accomplish the fast polymerization under UV irradiation to keep the printed patterns.

Based on the wide tuning range in reflection wavelength of the current mechanochromic photonic paper, multi-colored printing can be realized by controlling the degree of deformation in selected regions. As a demonstration, four squares with different colours are printed on the same red photonic paper with initial reflection wavelength of about 620 nm and reflection intensity of about 25%. Here, the photonic paper is a circular PC film with diameter of 15 mm and thickness of 180 μm, and the square printing plate is cut from silicon wafer with side length of 5 mm. As shown in digital photos (SI Fig 1), yellow, green, bluish green and blue squares can be printed on the red paper as the applied pressure is tuned from 20, 50, 100 to 140 kPa. In optical microscope images, the red colloidal microcrystals change their color under deformation due to the shrinkage of photonic crystal lattice. (Fig 2a-2d) Corresponding reflection spectra show that the reflection wavelength of the deformed region gradually blue shifts from about 620 nm to 590, 565, 517 and 492 nm while those of the undeformed regions remain unchanged after printing, which forms the color contrast to show the pattern. (Fig 2e-2h) Along with the blue shift of reflection, its intensity decreases and the peak width becomes wider, which

is resulted from the gradual losing of degree of order for colloidal microcrystals as stronger external force is applied. With a wedge-shape printing plate, a photonic crystal grating with continuously changed structure colors and reflection peaks can be easily obtained using current method. (SI Fig 2)

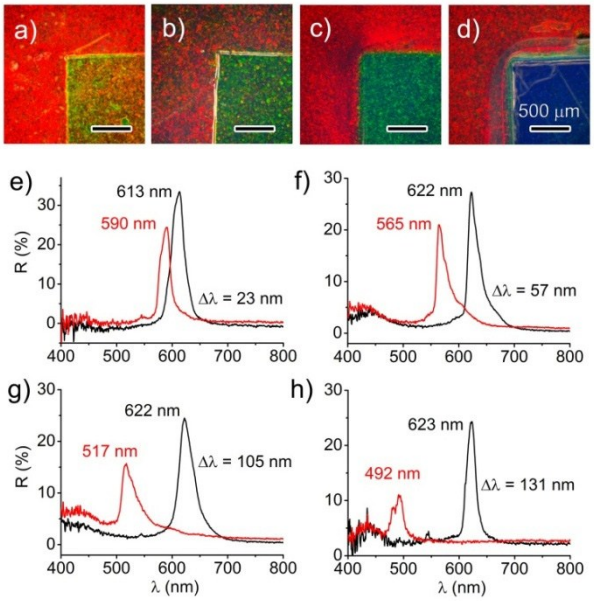

Fig 2. Optical microscopic images of a) yellow, b) green, c) bluish green and d) blue squares printed on the red photonic paper and e-h) reflection spectra for the deformed (red line) and undeformed (black line) photonic structures.

The relief printing method is capable of creating high resolution patterns on the photonic paper. Here, a polydimethylsiloxane (PDMS) replica of an anti-reflection film is used to test the resolution. As shown in microscopic image (Fig 3a), the PDMS stamps are composed of hexagonally arranged concave triangular cones, whose side length and height are 180 and 55 μm, respectively. The original photonic paper is composed of large number of green colloidal microcrystals. (Fig 3b) When the PDMS stamp is pressed to the photonic paper with pressure of 35 kPa, a hexagonal array of green triangles separated by blue edges shows up immediately, which is then fixed permanently by UV irradiation. (Fig 3c) It proves that microscale patterns with sharp edges can be printed only if a qualified printing plate or stamp is available. In the amplified microscope image (Fig 3d), one can find that the line resolution of the pattern has reached about 10 μm, which is seldom reported in previous research works.

The high resolution of current photonic printing process originates from the exact mechanochromic response of the used photonic paper to the localized deformation in microscale range. In this work, the gel-like SiO_2/EG-PEGMA photonic paper is composed of SiO_2 colloidal microcrystals and amorphous stacking of SiO_2 particles, where the average diameter of microcrystals ranges from 20 to 80 μm. It may not be difficult for the resolution to reach about 80 μm using proper stamps. However, people are curious about the precision of mechanochromic response if the designed pattern is smaller than the size of microcrystals. Our experimental results show that when the deformation goes across the microcrystal, it displays red and green structural color in the same microcrystal with an obvious boundary. (SI Fig 3) This clearly indicates that the resolution is not restricted by the size of microcrystal but only determined by the dimension of the stamp. Furthermore, the high resolution is not affected by the observation angle either although the structural colors blue shifts at large angles. (SI Fig 4) Compared to the well-developed ink-jet photonic printing, which prints patterns based on the contrast between in situ prepared photonic crystals and substrate, the current relief printing method does not involve the formation of photonic crystals during printing. Therefore the saturation of structural colors, determined by the intensity of reflection, will not decrease as the printed feature approaches micrometer size, which provides a good supplementary method when high resolution is desired.

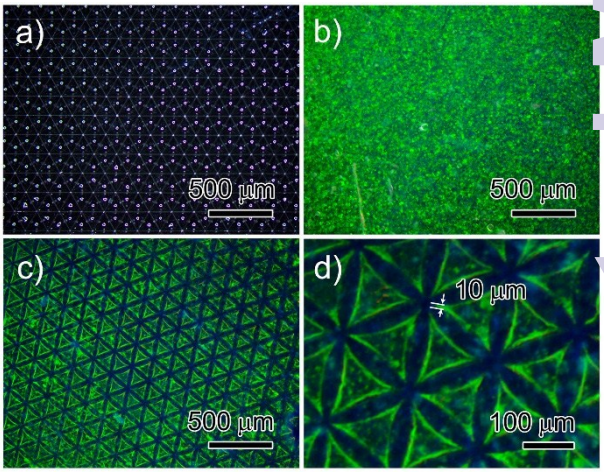

Fig 3. Optical microscope images of a) PDMS stamp with concave triangular cones, b) green photonic paper and c, d) hexagonal array of micro triangles printed on paper.

The high resolution feature of the relief style photonic printing also brings potential application in our daily life, such as the fingerprint recognition. (Fig 4) Generally, a human fingerprint is composed of arc-line “ridges” and “valleys” with average spacing of several hundred micrometers. For the mechanochromic photonic paper composed of red colloidal crystals, it shows typical reflection at 630 nm throughout the whole paper. Here, the microscopic reflection spectrum is measured by a spectrometer coupled to the optical microscope, which shows the localized reflection signal of colloidal microcrystals in a circular field of vision with diameter of 50 μm. As the finger pressed onto the photonic paper, the homogenous photonic crystal film separates into two parts immediately, which precisely reproduce the fingerprint patterns. It is easy to understand that the film pressed by the “ridges” turns green and its corresponding reflection blue shifts to 567 nm, since the crystal lattice shrinks in the vertical direction due to pressing. Meanwhile, the film touching the “valleys” keeps red and its reflection slightly red shifts to 65[illegible] nm, because this part of the film is horizontally squeezed by the neighboring ridges during pressing and the crystals lattice expands in the vertical direction. The PC film can be reversibly

used to show the fingerprints in real time which can be recorded by digital camera. (Video in SI) Fixing the deformed PC film will produce permanent fingerprints, but the process needs to be optimized to realize fast polymerization by weak UV light for safety considerations.

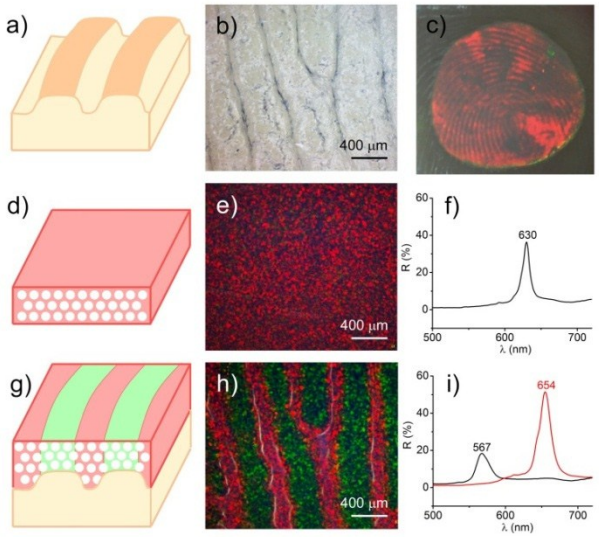

Fig 4. Schematic illustrations and optical microscope images of a, b) finger, d, e) red photonic paper and g, h) fingerprints produced by pressing the finger on photonic paper. c) Digital photo of a typical fingerprint. Microscopic reflection spectra of f) the original photonic paper and i) the "ridge" (black line) and "valley" (red line) section of the fingerprints on photonic paper.

In summary, SiO_2 colloidal particles, EG and PEGMA are used to fabricate mechanochromic photonic crystal film, and a new photonic printing method combining the old relief printing technique with the photo polymerization is developed to prepare multi-color or high resolution photonic patterns. The sensitive mechanochromic response and the fast curable characteristic of the photonic paper are the keys to accomplish the printing. The wide tuning range in structural color for the current paper under deformation helps to realize multi-color printing. While, the localized deformation among or even inside the colloidal microcrystals renders the photonic paper exact and high resolution mechanochromic response to sophisticated printing plates.

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