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Supporting Information

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

Dongpeng Yang,[a, b, †] *Siyun Ye*[a, †] *and Jianping Ge*[a, *]

a. Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, P. R. China, 200062.

b. Department of Chemistry, Tongji University, Shanghai, P. R. China, 200092

† These authors contributed equally to this work.

E-mail: jpge@chem.ecnu.edu.cn

Experimental Section

Materials: Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (28%) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Carbon black (99.5%, 30 nm) was purchased from Aladdin Co. Ltd.. Ethylene glycol (EG, 99%) and ethanol (99.9%) were purchased from J&K Co. Ltd.. Poly(ethylene glycol) methacrylate (PEGMA, Mn=360) and poly(ethylene glycol) diacrylate (PEGDA, Mn=700) was purchased from Sigma-Aldrich. Silicone elastomer base and curing agent (Sylgard 184) were obtained from Dow Corning. All chemicals were used directly as received without further purification.

Preparation of Photonic Crystal Paper: In a typical process, an elastic SiO_2/EG-PEGMA photonic paper was prepared by fixing the metastable SiO_2 colloidal microcrystals in the matrix of EG and PEGMA through photo-polymerization. Monodisperse SiO_2 particles with a diameter of ~200 nm were first synthesized by Stöber method. SiO_2 particles (0.08 cm^3, equals 80 μL) dispersed in ethanol (1.0 mL) were mixed with EG (77 μL) and PEGMA (43 μL). After being evaporated at 90 °C for 2 hours and cooled down to room temperature, the mixture was concentrated to a homogeneous solution (200 μL) and 30 μL of the liquid suspension was sandwiched between two glass slides separated by an interval of 0.18 mm and placed without disturbance for 10 min to form a metastable colloidal crystal precursor, which was further cured by UV light (365 nm, 4.8 mW/cm^2) for 20 min to generate a mechanochromic photonic paper.

Printing the Photonic Crystal Pattern: The photonic paper was soaked with the mixture of PEGDA and EG (1:1, 30 μL) for 2 hours, peeled off by a razor blade and transferred onto a glass slide or a carbon nano powder doped polydimethylsiloxane (PDMS) rubber. The as-made photonic paper was then pressed by rubber stamps like most relief printing operations, so that the raised pattern was displayed on the photonic paper due to nonuniform deformation. At the same time, the crosslinker swelled photonic paper was cured by UV light for 20 seconds to fix the photonic structures of the paper, so that the pattern was permanently recorded.

Characterization: The reflection spectra were measured by an Ocean Optics Maya 2000 Pro fiber spectrometer coupled to a six-around-one reflection/back scattering probe, where both the incident and reflective angle were fixed at 0°. Generally, the optical probe collected reflection signals within a circular region with a diameter of about 4 mm. The optical microscope images were taken by an Olympus BXFM reflection-type microscope operated in dark-field mode.

Calculation of Lattice Constants

When the incident light is parallel to the normal direction of the photonic paper, the diffraction wavelength (λ) can be calculated by equation (1). The effective refractive index (n_{eff}) of the composite film can be calculated by equation (2) as a weighted sum of the refractive indices (n_i) of each component, where V_i is its corresponding volume ratio.

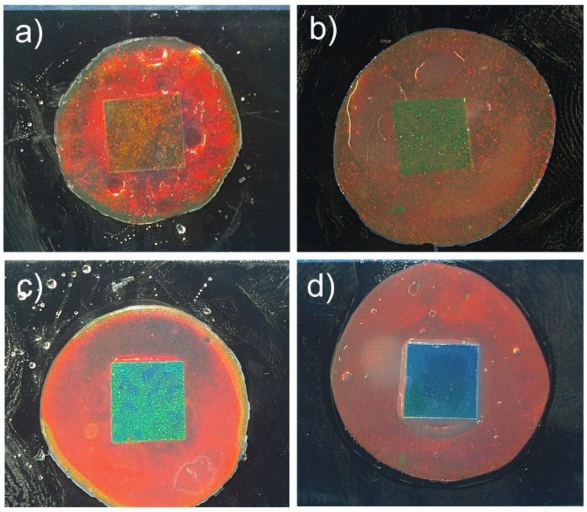
$$\lambda = 2 \times n_{eff} \times d \quad (1)$$

$$n_{eff}^2 = \sum n_i^2 \times V_i \quad (2)$$

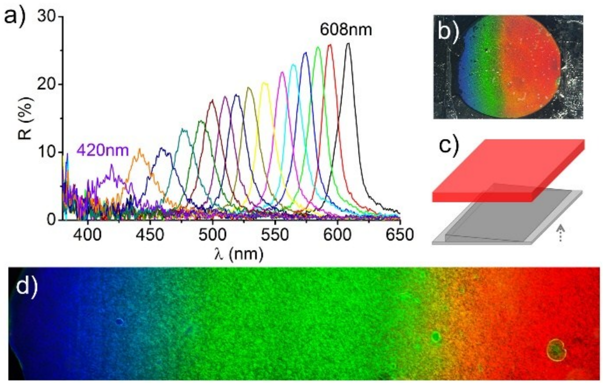
The refractive indexes of SiO_2, EG, PEGMA are 1.45, 1.43 and 1.46. The initial volume ratios of SiO_2, EG, PEGMA in the photonic paper are 0.4, 0.385 and 0.215. So the n_{eff} is calculated to be 1.44, and it can be considered as unchanged during the printing because the addition of PEGDA and EG won't change the refractive index too much.

$$n_{eff} = \sqrt{1.45^2 \times 0.4 + 1.43^2 \times 0.385 + 1.46^2 \times 0.215} = 1.44$$

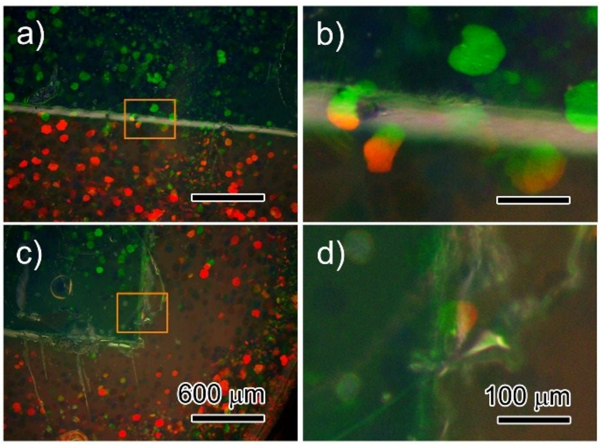
For the original red photonic paper, according to its wavelength (622 nm), the lattice constant (d) is calculated to be 216 nm by equation (1). For the green photonic paper (565 nm) and blue photonic paper (492 nm), the lattice constants are calculated to be 196 and 171 nm, respectively. The calculated values are larger than the observed lattice constants (179, 161, 152 nm), because the evaporation of EG during SEM sample preparation will decrease the lattice constant of photonic crystal gel.



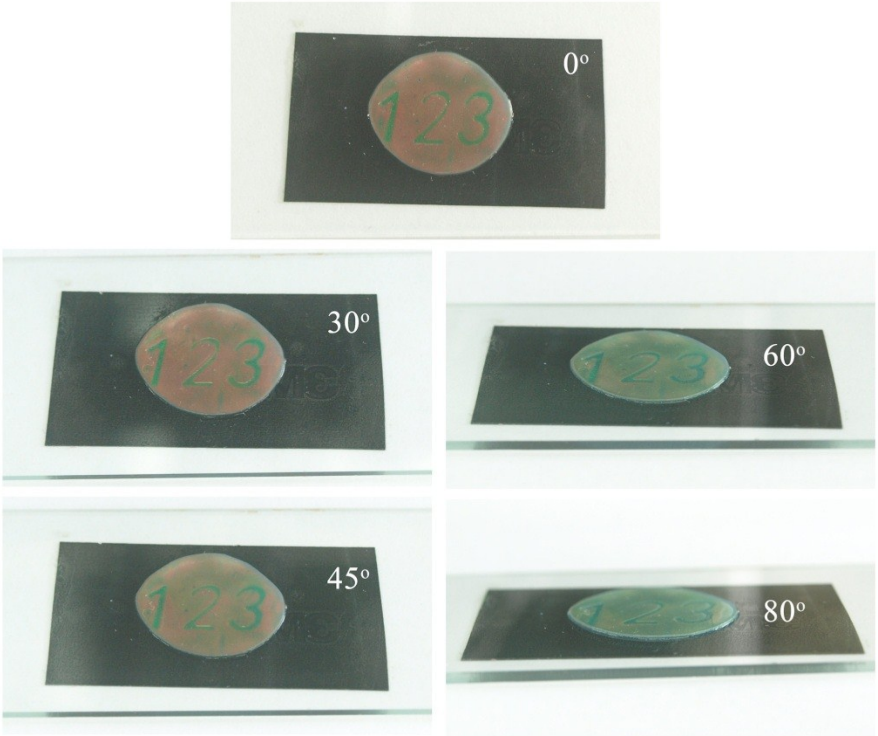
SI Figure 1. Digital photos of a) yellow, b) green, c) bluish green and d) blue squares printed on red photonic paper.



SI Figure 2. a) Spectrum, b) digital photo and d) optical microscope image of a photonic crystal grating printed by c) a wedge-shape printing plate.



SI Figure 3. The contrast of structural color generated inside a single colloidal microcrystal due to accurate mechanochromic response to the localized deformation.



SI Figure 4. Digital photo of the photonic prints with observation angle changing from 0, 30, 45, 60 to 80°.