# Revealing invisible photonic printing: colorful pattern shown by water

**C Chen[1], Z Q Dong[1], Y Chen[1], X B Hu[1], X R Zhu[1], Z G Zhu[1,4], S H Qian[2] and W H Shih[3]**

[1]School of Environmental and Materials Engineering, College of Engineering, Shanghai Polytechnic University, Shanghai 201209, P. R. China
[2]Department of Ophthalmology, Eye and ENT Hospital, Shanghai Medical College, Fudan University, Shanghai 200231, P. R. China
[3]Department of Materials Engineering, Drexel University, Philadelphia, Pennsylvania 19104, United States

E-mail: zgzhu@sspu.edu.cn

**Abstract.** Patterning and displaying of photonic crystals are critical for building advanced photonic materials. We developed a monolayered colloidal crystal (MCC) based photonic material through a mask-assistant photo-polymerization process. Polystyrene (PS) nanoparticles were firstly assembled on the glass slide to form highly ordered MCC, this template is invisible and could diffract visible light when infiltrated by solvent. This reversibly displaying property was successfully maintained after the MCC was surrounding by a polymer layer *via* photo-polymerization, meanwhile a pattern could also be printed on the polymer with the help of a mask. Such photonic printing could be reversibly shown and hidden, revealing the colorful pattern was mainly due to the non-uniform cross-linking density of the polymer.

## 1. Introduction

Photonic crystal (PC) materials have been considered to be one of the promising candidates for advanced photonic devices of the next generation due to whose prominent light trapping and waveguiding properties. As periodically ordered assembly of monodispersed colloidal particles, colloidal crystals (CC) have demonstrated to possess a region of forbidden frequencies in transmission is known as the photonic band gap (PBG)[1]. These crystalline PBG materials have potential for a wide variety of applications including chemical sensing, displaying, anti-counterfeiting, and antireflective coatings [2-5]. To achieve advanced photonic devices, many techniques have been developed for rapid, convenient and large-scale production of CCs in three-dimensional (3D) and two-dimensional (2D), such as spin-coating, interfacial assembly, and convective assembly [6-9].

For 3D CCs, extensive attentions have been focused on the fabrication of opal and inverse opal structures [10]. The 3D CCs could be embedded in a hydrogel whose volume change leads to the change of the CC lattice, and thus shift the Bragg diffraction wavelength. As the hydrogel was functionalized for recognition of the analytes such as glucose, pH, certain solvents and heavy metal cations, the hydrogel swell or shrink according to the concentration of the analytes could be transformed to the color change [11-15]. On the other hand, 2D CCs, which are monolayered architectures of colloidal particles distinguished from 3D ones, have also attracted intensive research

interest due to their unique properties as PBG materials, or as templates in engineering of 2D arrays of various nanostructures [16, 17].

Patterning and displaying of photonic crystal materials are critical in building advanced photonic devices. In this paper, we report an invisible photonic printing based on monolayered colloidal crystal (MCC) that can easily shown by water. MCC was firstly self-assembled onto a glass slide *via* a classic horizon evaporation method [18, 19]. A layer of hydrogel was *in situ* photo-polymerized upon this 2D crystal to form a polymerized MCC (PMCC). The pattern of the PMCC photonic material was printed through a mask during the polymerization process. This technology enables the convenient fabrication of invisible printing with a 2D photonic crystal, allowing the fast preparation of PMCC materials.

## 2. Experimental

### *2.1. Chemicals and Materials*

Styrene (St, 99%), sodium hydrogen carbonate ($NaHCO_3$, 99.5%), ammonium persulfate (KPS, 98%), acrylamide (AMD, 98.5%), N,N'-methylene-bisacrylamide (MBA, 98%), hydrogen peroxide ($H_2O_2$, 30%), ethanol (99.7%) and acetone (99.5%) were purchased from Shanghai Chemical Agent Co., Ltd. 2,2-Diethoxyacetophenone (DEAP, 98%) was purchased from Acros Organics. All chemicals were used as received without further purification. The glassware used in all experiments was cleaned in $H_2O_2$ solution for 30 min.

### *2.2. CC Preparation*

Monodisperse polystyrene (PS) nanoparticles with diameter of 400 nm were prepared by emulsifier-free polymerization using St as monomer, $NaHCO_3$ as buffer and ammonium persulfate (98%, Shanghai Chemical Agent Co., Ltd) as initiator. Detailed reaction procedure was described elsewhere [20]. The resulting latex was dialyzed against ultrapure water (18.2 MΩ cm) for 7 days to remove the excess ions, and PS particles were diluted with ethanol after purification ($V_{latex}$:$V_{ethanol}$=1:3). Monolayered CC was assembled from ethanol-diluted PS particles on a glass slide by utilizing a horizon evaporation method [21]. The glass slide was wetted with water and 5 μL diluted PS was injected onto the slide, and a layer of PS CC was formed rapidly on the air-liquid interface. After the solvent was removed by evaporation, the sample was treated in an oven at 80 °C for 2 h.

### *2.3. PMCC Preparation and Patterning*

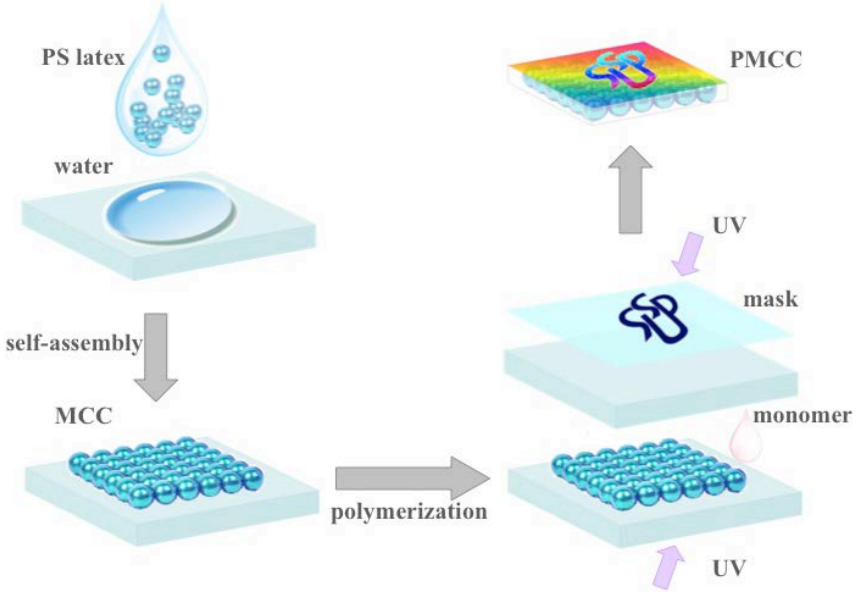


**Figure 1.** Schematic representation of the preparation of PMCC.

In a typical recipe, 0.702 g AMD and 0.003 g MBA (monomer and cross-linker, respectively, in a molar ratio of 50:1) were mixed and dissolved in 3 mL water in a sample vial, and 5 μL DEAP was added as photo-initiator, and the mixture was agitated and then carefully injected onto the MCC layer. Another glass slide with a mask was covered onto the mixture and MCC supporting slide, and the system was exposed to a set of UV light from Black Ray (365 nm) mercury lamps from both sides of the coupled slides for 40 min to form PMCC. The resulting photonic hydrogel film could be peeled off from the glass slide and washed with ultrapure water. The route for the fabrication of PMCC is illustrated in Figure 1.

*2.4. Characterization*

The optical data of photonic films were collected with a fiber optic spectrometer (USB 4000-XR1-ES, Ocean Optics). Spectra were captured between the wavelengths of 350 and 900 nm. The diffraction characteristic could be accurately predicted through Bragg's relationship:

$$m\lambda_0 = 3^{1/2} d\sin\theta \quad (1)$$

where m is the diffraction order, $\lambda_0$ is the diffracted wavelength, $d$ is the nearest spacing of the monolayered particle, and $\theta$ is the angle of the light relative to the normal to the MCC, during diffraction the $\theta$ is ~19°.

Structural and morphological characterizations of the crystals were performed using a field emission scanning electron microscope (FESEM, S-4800, Hitachi) operating at an acceleration voltage of 10 kV, the samples were sputter coated a thin layer of Au.

## 3. Results and Discussion

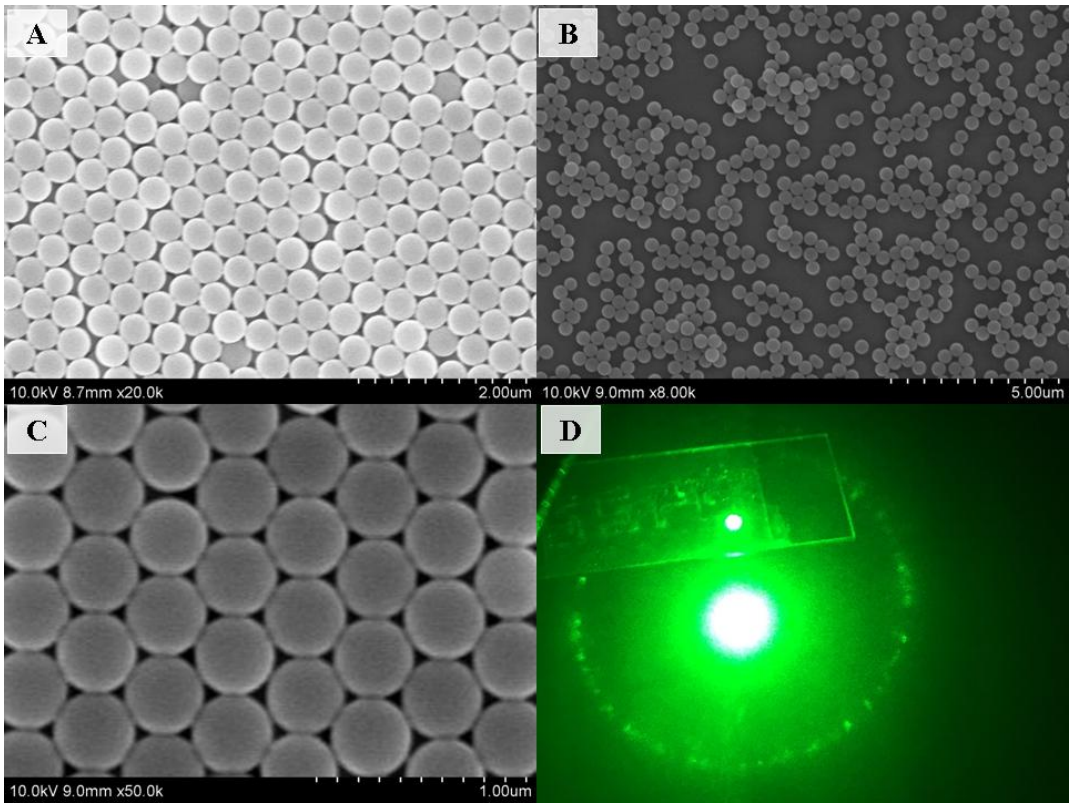


**Figure 2.** SEM images of the assembled PS particles at various evaporation conditions: (A) 100 °C heating, (B) nitrogen flow, and (C) ambient temperature. (D) Debye ring diffraction from the MCC irradiated by a green laser.

The work presented here describes the combination of polyacrylamide (PAMD) hydrogel and monolayered colloidal crystal (MCC) to form a polymerized monolayered colloidal crystal (PMCC) photonic crystal (PC) material. The MCC consists of an assembly of spherical polystyrene (PS) particles constructed into a generally hexagonal-close-packed (HCP) lattice such that the system minimizes its free energy. This ordered structure of could be coupled with a hydrogel matrix *via* an *in situ* photo-polymerization to form a more stable PMCC, where the MCC lattice distance, and accordingly the diffraction wavelength, reports the hydrogel volume shifting. In contrast to traditional 3D polymerized CC, 2D PMCC readout should be intrinsically more sensitive and reliable since the 2D diffracted wavelength is independent of the refractive index [22].

*3.1. Self-Assembly Condition*

Monodispersed colloidal spheres can be self-assembled into large-area CCs with high quality by a variety of methods. We compared evaporation conditions upon morphology of the PS assembly. As shown in Figure 2A, the sample was put on a heater at 100 °C for several seconds to remove the solvent, the PS particle readily assembled into multilayered structures since the air-liquid interface was disturbed by the ultrafast dehydration of the system, and the particles stacked repeatedly leading in a 3D ordered CC [23]. By applying gentle nitrogen flux on the top of the sample to promote the evaporation (Figure 2B), on the other hand, resulted in a 2D disordered diluted sub-monolayer. Although the assembling of PS particles on the gas-liquid interfaces was visually evidenced, the fast removal of the solvent caused the disturbance of the PS particles, and then randomly scattered across the substrate due to the capillary immersion that attracted each other, hence no continuously ordered array could be found. Figure 2C confirms a structure with long-distance order and hexagonal symmetry of the sample prepared at the natural assembly speed, long-distance ordered structure. The structure of the MCC was also studied by laser diffraction, a convenient method to confirm 2D array and it's particle spacing. If the particles form a perfect hexagonal 2D array, a diffraction of 6-spots symmetry will be shown when illuminated with monochromatic laser light. If the 2D CC exposed in laser beam is randomly oriented, since the crystallites are significantly smaller than the beam, many symmetry spots with the same diffraction diameter will form a ring, such diffraction pattern is called Debye ring [19]. We excite the MCC along its normal with a 532 nm laser pointer and the 2D crystal array diffracts the light depend on the particle spacing and the laser wavelength. As expected, a sharp circle was observed.

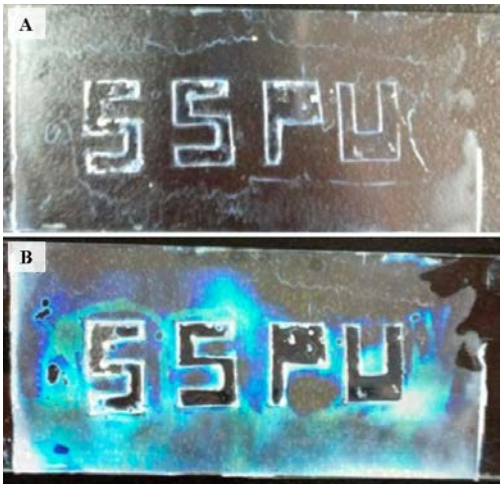


**Figure 3.** Photograph of (A) invisible MCC coating and (B) MCC coating with "SSPU" pattern shown by solvent.

The as-prepared MCC was shown in Figure 3A, we cut the word "SSPU" with parafilm (~125 μm thick) and covered on the glass slide, After MCC coating, the parafilms were peeled off from the slide and the covered part remain uncoated. The diffraction of the 2D array in air is in the UV region and thus cannot be visualized. The pattern could be easily shown by slightly swelling the PS particles with acetone, as shown in Figure 4b, the image of the word "SSPU" whose area excluded the MCC coating could be easily distinguished. As the diffraction of 2D array is unrelated to refractive index, the red-shift of the MCC from UV to visible region is caused by the increasing packing density due to the swelling of the PS particles.

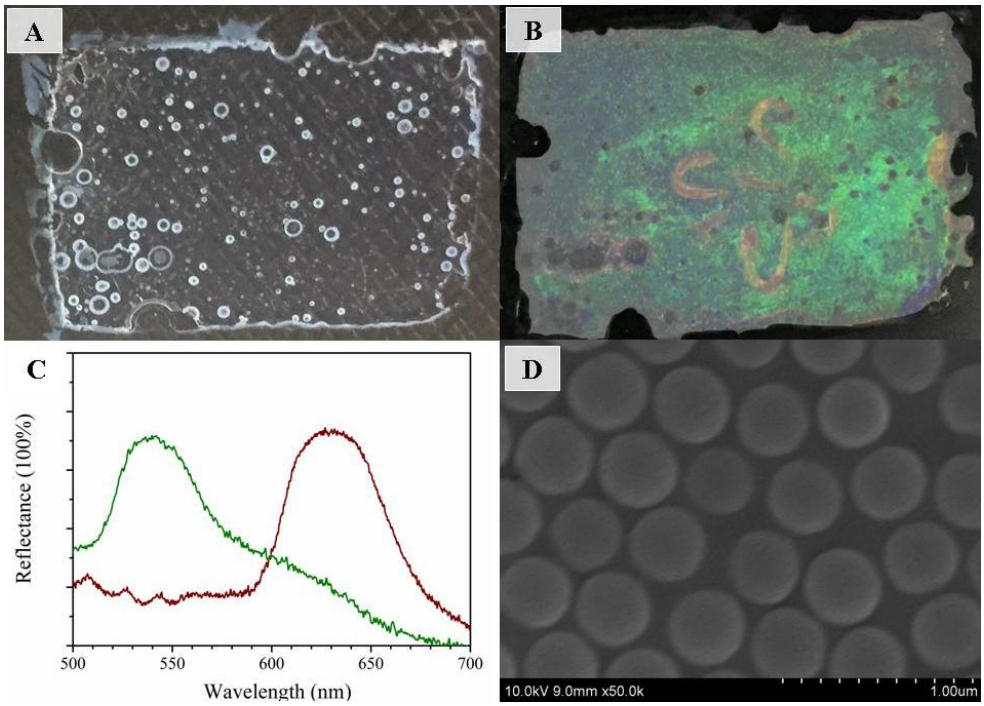


**Figure 4.** Photograph of PMCC at (A) dehydration state and (B) rehydration state; (C) reflection spectra of different parts of the rehydrated PMCC; and (D) SEM image of the PMCC.

It is a facile method to combine the MCC with a hydrogel, which is significantly different from the 3D CC based hygrogels. Since the ionic species could disorder the 3D array, the ionic monomers cannot be directly utilized for the formation of the hydrogel. To solve this limitation, physically gelated hydrogels were studied, which allows exclusively variation in the shape and thickness of the PC materials, however, the preparation need several hours or even longer for the subsequence modification [24-26]. The 2D CC, without the electrostatic force between layers, could be combined with nonionic monomers as well as ionic ones.

We *in situ* photo-polymerized AMD upon the MCC to form a PAMD PMCC. During the polymerization, a mask with pattern of "SSPU" logo was covered on the glass slide, and thus the pattern was printed on the PMCC due to the different degrees of polymerization. Figure 4A shows the photograph of the as-prepared PMCC, the hydrogel is transparent and the diffraction of MCC is in UV, thus the pattern is invisible. The photonic patterns in dried state could be revealed by water immersion due to the non-uniform change in photonic structure. As shown in Figure 4B, the swelled PMCC clearly displayed the pattern "SSPU" in red while other area displayed green, these two parts have very close photonic structures but different swelling capabilities, because the usage of the mask led to different crosslinkages of the polymer hydrogel, so that they could generate a large color contrast as they swell differently. Once the sample is dried, the PMCC changes back to invisible state, and such displaying is fully reversible. The sample could instantly and reversibly show the patterns by

rehydration and hide by dehydration for many times. We measured the reflection spectra of the swollen PMCC (Figure 4C), the pattern reflected ~ 632 nm while the green part reflected ~ 540 nm, the different crosslinking levels made the pattern and the background both invisible at dehydrated state but a $\Delta\lambda$ (~100 nm) under rehydration, this high resolution was accomplished by the optimization of the printing time during the polymerization process based on the relationship between crosslinking level and the reflection changes during rehydration. We also examined the microstructure of the PMCC material, as can be seen in Figure 4D, we found that the 2D layer was well conjugated with the hydrogel except that the close-packed structure was converted into a slightly non-close-packed form after the polymerization. This might be the relaxation of the PAMD molecule chain after the polymerization was quenched. It took ~100 s for the revealing of the pattern, the response time is faster than those 3D CC hydrogels [15].

## 4. Conclusions

In conclusion, we fabricated two-dimensional photonic crystal material by first assembling the polystyrene nanoparticles into monolayered colloidal crystal at air-liquid interface, followed by polymerizing a hydrogel layer and a specific pattern could be printed under UV irradiation. The construction of PMCC maintaining highly ordered 2D array structure and the key point of the patterning technique is controlling the crosslinking density so that a non-uniform change in photonic structure could be realized under rehydration. The PMCC was initially transparent and a sharp resolution with a red pattern (~ 632 nm) and green background (~ 540 nm) could be observed by water immersion. Our progress enables the convenient fabrication of invisible printing with a 2D photonic crystal, allowing the fast preparation of PMCC materials. This printing technique is capable of creating invisible photonic prints that could be easily shown and hidden, we anticipate such PMCC would found potentially use in applications for sensing, security printing and anti-counterfeiting purpose.

**Acknowledgments**

This work was supported by the National Natural Science Foundation of China (61471233, 21504051), the Program for Professor of Special Appointment (Eastern Scholar) at SIHL, the Sailing Project and Basic Research Program from Science and Technology Commission of Shanghai Municipality (14YF1410600, 14JC1406402), Shuguang and ChenGuang project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (14SG52, 13CG62), the key subject of Shanghai Polytechnic University (Material Science and Engineering, XXKZD1601).

**References**

[1] Zhao Y, Shang L, Cheng Y and Gu Z 2014 *Accounts Chem. Res.* **16** 3632
[2] Ge J and Yin Y *Angew.* 2011 *Chem. Inter. Edit.* **50** 1492
[3] Ye S, Fu Q and Ge J 2014 *Adv. Funct. Mater.* **24** 6430
[4] Zhang Y, Tang B, Wu Z, Shi H, Zhang Z and Zhao G 2016 *Green Chem.* **18** 2424
[5] Heo E, Kang H, Lee J, Oh Y and Kim S 2016 *Small* **28** 3819
[6] Ye X and Qi L 2014 *Sci. China. Chem.* **1** 58
[7] Xia Y, Gates B and Li Z 2001 *Adv. Mater.* **13** 409
[8] Mastrangeli M, Abbasi S, Varel C, Hoof C, Celis J and Böhringer K 2009 *J. Micromech. Microeng.* **19** 083001
[9] Freymann G, Kitaev V, Lotsch B and Ozin G 2013 *Chem. Soc. Rev.* **42** 2528
[10] Marlow F, Muldarisnur, Sharifi P, Brinkmann R and Mendive C 2009 *Angew. Chem. Int. Ed.* **48** 6212
[11] Fenzl C, Hirsch T and Wolfbeis O 2014 *Angew. Chem. Int. Ed.* **53** 3318
[12] Cullen D, Xu Y, Reneer D, Browne K, Geddes J, Yang S and Smith D 2011 *Neuroimage* **54** S37
[13] Galisteo-López J, Ibisate M, Sapienza R, Froufe-Pérez L, Blanco Á and López C 2011 *Adv.*

*Mater.* **23** 30
[14] Lee J, Jin H, Desai M, Ren S, Kim S and Lee S 2015 *Nanoscale* **7** 18379
[15] Lu W, Asher S, Meng Z, Yan Z, Xue M, Qiu L and Yi D 2016 *J. Hazard. Mater.* **316** 87
[16] Jing P, Wu J and Lin L 2014 *ACS Photonics* **1** 398
[17] Ye X and Qi L 2011 *Nano Today* **6** 608
[18] Alfrey T Jr, Bradford E, Vanderhoff J and Oster G 1954 *J. Opt. Soc. Am.* **44** 603
[19] Prevo B and Velev O 2004 *Langmuir* **20** 2099
[20] Chen C, Zhu Z, Shih W, Ge Q, Liu M and Zhu X 2015 *J. Nanosci. Nanotech.* **15** 3239
[21] Denkov D, Velev O, Kralchevski P, Ivanov I, Yoshimura H and Nagayama K1992 *Langmuir* **8** 3183
[22] Kanai T, Sawada T and Kitamura K 2003 *Langmuir* **19** 1984
[23] Gallego-Gómeza F, Morales-Flórezb V, Moralesa M, Blancoa A and Lópeza C 2016 *Adv. Colloid. Interfa.* **234** 142
[24] Chen C, Zhu Y, Bao H, Zhao P, Jiang H, Peng L, Yang X and Li C 2010 *Soft Matter* **7** 915
[25] Chen C, Zhu Y, Bao H, Shen J, Jiang H, Peng L, Yang X, Li C and Chen G 2011 *Chem. Commun.* **47** 5530
[26] Chen C, Zhu Z, Zhu X, Yu W, Liu M, Ge Q and Shih W 2015 *Mater. Res. Express* **2** 046201