Supporting Information to:

Large-scale colloidal films with robust structural colors

Jing Zhang, Zhijie Zhu, Ziyi Yu, Luting Ling, Cai-Feng Wang and Su Chen**

A. Materials and Methods

1.1 Materials

Polyvinylpyrrolidone (PVP, K 30), ethylene glycol (EG), water-borne polyurethane (solid content 35 wt%, specification model: 718, Jining Baiyi Chemical Co., Ltd) and polyvinyl alcohol (PVA, polymer degree = 1750 ± 50, 87-89% hydrolyzed) were purchased from standard sources and used as received. PVA was dissolved in deionized water at 85 ^{o}C to form 5 wt% PVA solution before use. Styrene (St) was purified by distillation under reduced pressure to remove inhibitors. The initiator, potassium persulfate (KPS) was purified by recrystallization and stored in refrigerator until using. Purified water with resistance greater than 18 MΩ·cm was used in our experiments. The humidity for ink drying was recorded by a humidity meter (GM1361, Benetech Corp.) and adjusted by a commercially available humidity regulator coupled with steam humidifier (HQ-JS130H, Haoqi Electric Appliances Corp.).

1.2 Synthesis of polystyrene (PS) microspheres

Monodispersed PS microspheres were prepared *via* an improved emulsion polymerization method: high, near to boiling point temperature (98 ^{o}C) was used to assure high reaction speed. In specific, 4.5 - 8 g of St, and 0.24 g of PVP were mixed in 135 g of deionized water in a four-necked round-bottomed flask equipped with a water-cooled reflux condenser, a

mechanical stirrer, a nitrogen inlet and a thermometer. After the mixture was heated at 98 ^{o}C for 5 min, the polymerization reaction was then initiated by dropwise adding 0.04 g KPS disolved in 15 g deionized water within 30 min. The reaction was continued for another 2 h to give the final products. The products were filtered through 200-mesh nylon net to remove minor traces of large agglomerates, and subjected to dialysis utilizing the dialysis bag with a 100 000 g·mol^{-1} molecular weight cut-off in ultrapure water for 7 days.

Solid content was determined by measuring the mass of the PS colloid suspensions (m_1) and its dry weight (m_2). It was calculated as:

$$\text{Solid content (\%)} = (m_1-m_2)/m_1*100\%$$

1.3 Preparation of the printing inks

The white PS powder was obtained by freeze drying of the dialysis products. To prepare the printing inks, 0.15 g PS powder was redispersed into a mixture of 90 μL (~ 0.1 g) EG and 900 μL (~ 0.9 g) deionized water. This ink formulation was adopted in all experiments unless stated otherwise.

1.4 Generation of tiny latex droplets via inkjet printing

A commercially available inkjet printer (Jetlab 4, from MicroFab Corp., USA) was used for all the inkjet printing trials. The printer has two stroboscopic cameras: one is to observe the droplet formation from the nozzle, and the other mounted vertically with respect to the surface of the substrate holder, to observe the deposited ink droplets. The printer is capable of independent X, Y and Z-stage movement: the first two were to position the substrate holder, and the Z-stage, to adjust the distance between the print-head and substrate holder. The colloid deposits were printed by using piezo-actuated nozzle with inner diameters of 30, 50 and 70 μm. The substrate holder and the print-head could be independently heated to control the ink drying temperature. Silicon wafers, glasses, or plastic films were used as the printing substrates. Herein, the size of the colloid deposits was associated with many factors including

the nozzle diameters, surface properties of the printing substrates, the distance between the printhead and substrates, and printing parameters (applied voltage and frequency). Since the assembly behaviour of printing droplets with size ranging from 100 to 300 micrometres has proved to be dominated by the ink formulation, drying temperature and moisture (**Figure 2b** and **Figure S3**), hence, in this context, researches mainly focused on the following drying behaviour, instead of detailed printing parameters. It is worth pointing out that the ink formulation demonstrated above could all achieve stable droplet ejecting ahead of the printer nozzle, indicating they are adequate as inks for inkjet printing applications.

1.5 Generation of tiny latex droplet via spray painting

A gravity feed-type airbrush (HS-35, Haosheng pneumatic Mcahinery Co., Ltd) connected with an air compressor (AS18-2, Haosheng pneumatic Mcahinery Co., Ltd) was used for spray painting. The PS colloid suspension was put into the reservoir sitting atop the airbrush, and ejected toward the printing substrate via the air compressor with a pressure of *ca.* 50 PSI. The distance between the gun and substrate was 80 cm. The airbrush was moved in a line-by-line fashion at a speed of *ca.* 1 $cm \cdot s^{-1}$, with each stroke overlapping with the previously sprayed area. The interval time between each stroke is set at 5 min to avoid the formation of thin liquid layers and hence the continuous colloidal crystal film with angle-dependent optical properties.

1.6 Construction of 2-D colloidal crystal films via bar coating

Specifically, the printing ink containing concentrated PS colloids was quickly cast onto the A4-sized PET film, and spread with the 9 μm-depth spiral bar. After water evaporation, colloid crystal films displaying bright structural colours were attained. It takes only 35 seconds to achieve highly-ordered colloidal crystal structures.

1.7 Instrumentation

The microstructures of as-synthesized microspheres were examined by using transmission electron microscopy (TEM) (JEOL JEM-2100). The sample was placed on a copper grid,

which was left to dry before being transferred into the TEM sample chamber. Scanning electron microscopy (SEM) images were acquired on a QUANTA 200 (Philips-FEI, Holland) instrument at 20.0 kV. UV-Vis transmission and reflection spectra of the printed colloidal crystal patterns were measured by the optic spectrometer (Ocean Optics, USB4000). Photographs were taken with an optical microscope (ZEISS, Axio Scope A1).

B. Printing ink design

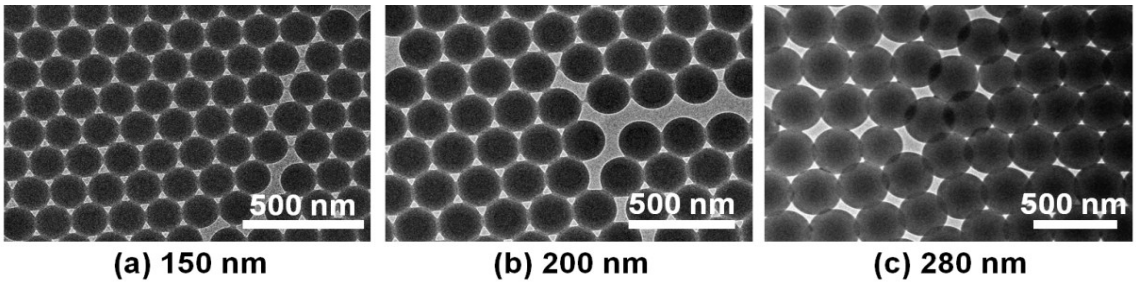

Figure S1. TEM images of the as-synthesized PS colloids. (a-c) Their corresponding DLS results were 195, 215 and 272 nm.

Monodispersed PS microspheres were prepared via an improved emulsion polymerization method. By adjusting the amount of styrene monomer, PS colloids with different diameters could be attained. As their typical SEM images show, these PS colloids were highly monodispersed with diameters ranging from 150, 200 to 280 nm, respectively.

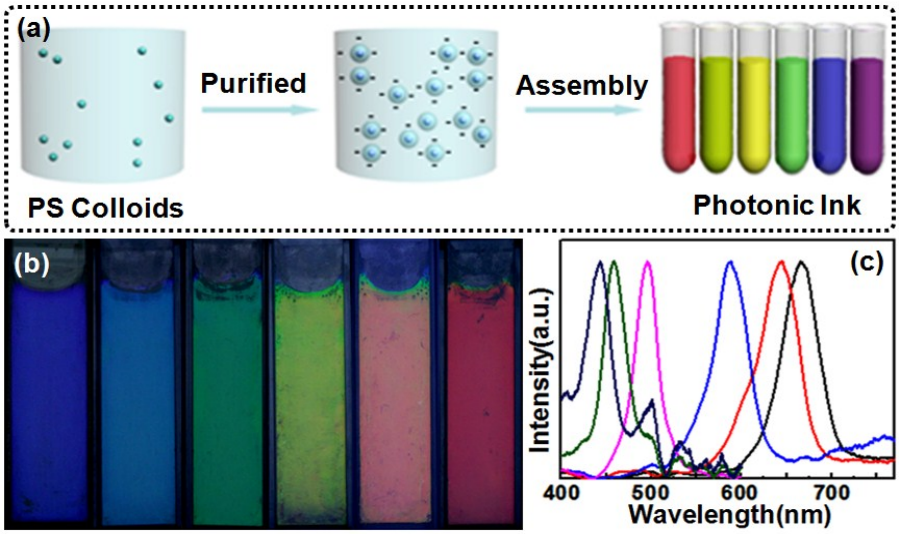

Figure S2. Preparation of the colloid printing ink. (a) Schematic illustration for the purification of the resulting colloid suspension via dialysis. The optical images (b) and corresponding reflection spectra of purified PS suspensions were given.

After the removal of the electrolytes via dialysis, the suspensions diffracted different colors due to the formation of crystalline colloidal arrays.

A concentration of 15 wt% PS colloids was chosen to prepare the printing ink. This is based on the following considerations:

1) Why not choose a lower colloid concentration?

   Previous researches clearly revealed that the particle concentration would produce an important change in the deposition patterns of the ink droplets on hydrophilic substrate (*Langmuir*, 2006, 22, 350). Accordingly, to obtain a complete layer of colloidal photonic crystal printing dot, the colloid concentration should not be less than 4%.

2) Why choose 15 wt%?

   Firstly, a concentration of 15 wt% PS colloids was determined by referencing literatures in this area (*Adv. Optical Mater.* 2014, 2, 34–38; *ACS Nano*, 2014, 8, 11094–11100.), so that the results could be easily compared, facilitating the unveiling of new phenomena or mechanisms.

   Secondly, the structural colour brightness or the refractive intensity of the printing patterns was highly relevant to the thickness of colloidal crystals, and hence taking into consideration its practical uses, high concentration PS colloids are preferred.

   Lastly, high concentrated colloids also facilitate the formation of colloidal skins. No colloidal skins were noticed when the PS colloid concentration was less than 10 wt%.

3) Why not choose an ultra-high concentration?

   This is because higher colloid concentration leads to higher viscosity, which would hazard the stability of the printing processes.

C. Structure and optical analysis of the resulting colloidal optical films

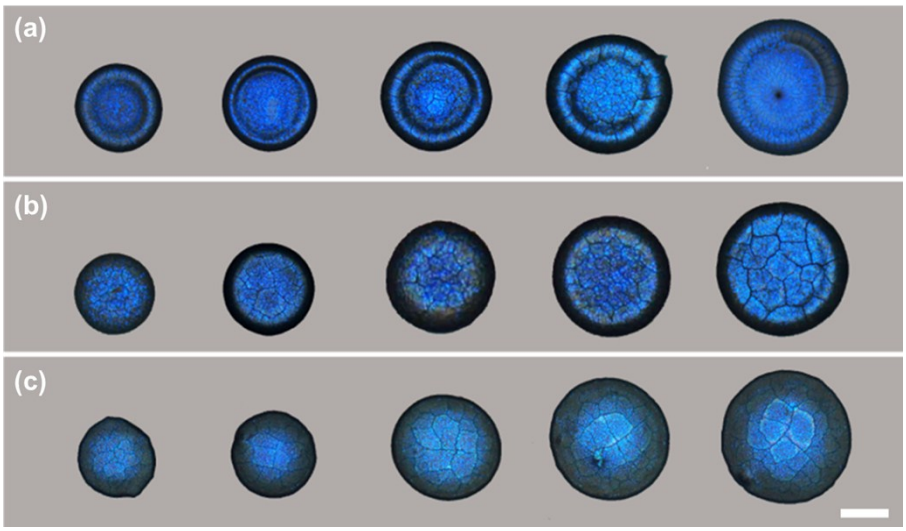

Figure S3. The optical images of the different sized printing dot series prepared by merely adjusting the printing nozzles or applied voltage. (a) The printing ink contains 15 wt% PS colloids and 85 wt% deionized water, and the printing droplets were dried under a temperature of 30 ^{o}C and relative humidity of 50 %. (b) The printing ink contains 15 wt% PS colloids, 10 wt% EG and 75 wt% deionized water, and the printing droplets were dried under a temperature of 25 ^{o}C and relative humidity of 40 %. (c) The printing ink contains 15 wt% PS colloids, 10 wt% EG and 75 wt% deionized water. and the printing droplets were dried under a temperature of 35 ^{o}C and relative humidity of 40 %. Scale bar = 100 μm.

The results show that the colloid deposit sizes could be tuned from *ca.* 100 to 300 μm through adjustment of the nozzle size or applied voltage. However, the sizes of deposited ink droplets have little effect on their final morphologies, and they were mainly determined by the ink formulation and drying temperature and humidity.

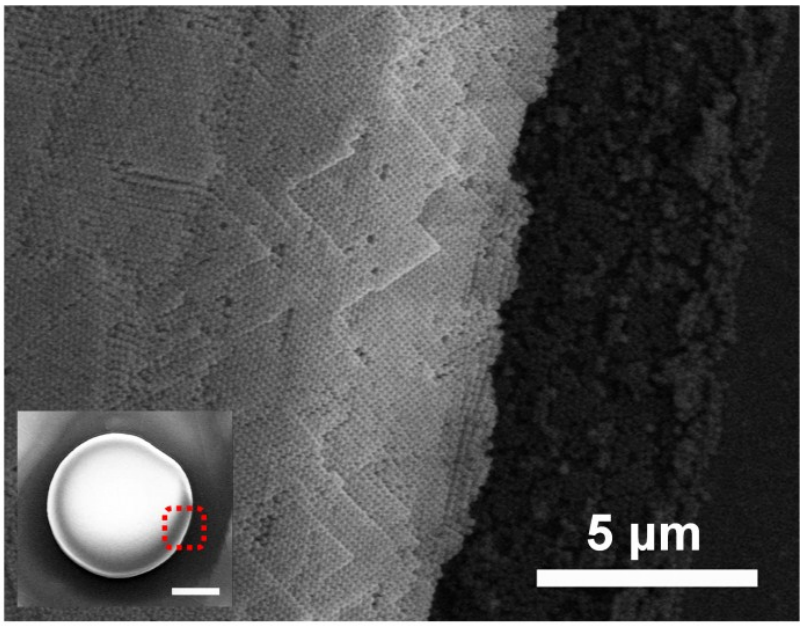

Figure S4. The SEM images of the uniform colloidal deposits. The drying temperature and humidity are 25 °C and 40%, respectively. The scale bar for the inset image is 50 μm.

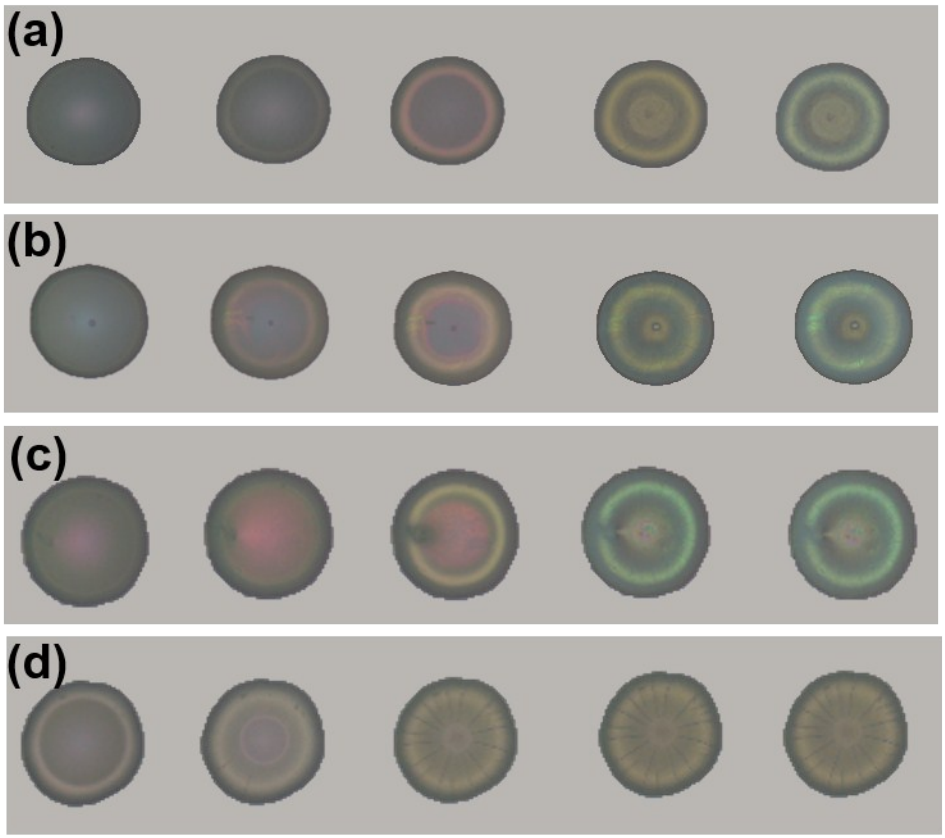

Figure S5. The real-time assembly processes of the ink droplets containing different concentrations of the PU polymers. (a) 0.35 wt% PU was added into the colloid ink containing 15 wt% PS colloids and 85 wt% deionized water. (b) 0.7 wt% PU was added into the colloid ink containing 15 wt% PS colloids and 85 wt% deionized water. (c) 1.75 wt% PU was added into the colloid ink containing 15 wt% PS colloids and 85 wt% deionized water. (d) 3.5 wt% PU was added into the colloid ink containing 15 wt% PS colloids and 85 wt% deionized water. The drying temperature and relative humidity were 30 ^{o}C and 40%, respectively.

The results show that the addition of PU into the colloid dispersion only could not eliminate the coffee ring effect.

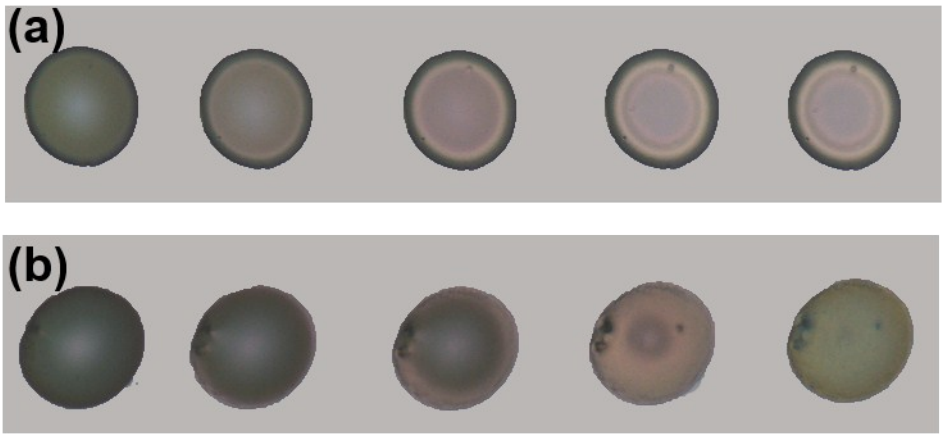

Figure S6. The real-time assembly processes of the ink droplets containing different concentrations of the PU and EG polymers. (a) 1.75 wt% PU was added into the colloid ink containing 15 wt% PS colloids 5 % EG and 80 % deionized water. (b) 1.75 wt% PU was added into the printing ink, which was made by dispersing 15 wt% PS colloids into a mixture of EG and deionized water (mass ratio = 1:9). The drying temperature and relative humidity were 30 ^{o}C and 40%, respectively.

Figure S6 show that the PU could not replace the role of EG in regulating the droplet drying processes. However, comparing to the printing ink without PU, the addition of minor PU into the printing ink would enhance the mechanical strength and decrease the mud cracks.

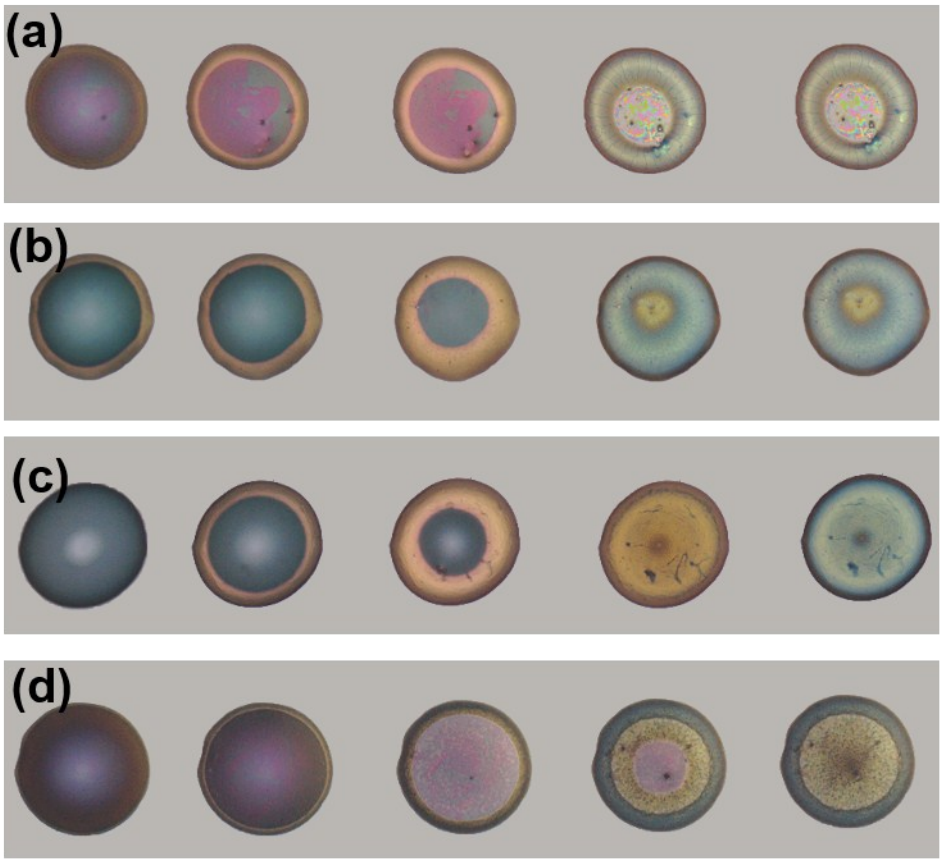

Figure S7. The real-time assembly processes of the ink droplets containing different concentration of PVA polymer. (a) 0.05 wt% PVA was added into the colloid ink containing 15 wt% PS and 85 wt% deionized water; (b) 0.1 wt% PVA was added into the colloid ink containing 15 wt% PS and 85 wt% deionized water; (c) 0.25 wt% PVA was added into the colloid ink containing 15 wt% PS and 85 wt% deionized water; (d) 0.5 wt% PVA was added into the colloid ink containing 15 wt% PS and 85 wt% deionized water; The drying temperature and relative humidity were 30 ^{o}C and 40%, respectively.

The results show that the addition of PVA into the colloid dispersion only could not eliminate the coffee ring effect.

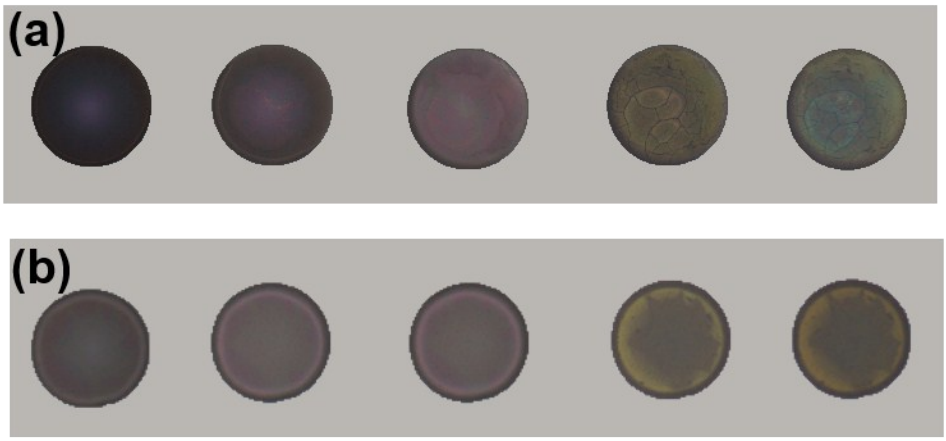

Figure S8. The real-time assembly processes of the ink droplets containing PVA and EG polymers. (a) 0.25 wt% PVA was added into the colloid ink containing 15 wt% PS colloids 5 % EG and 80 % deionized water. (b) 0.25 wt% PVA was added into the printing ink, which was made by dispersing 15 wt% PS colloids into a mixture of EG and deionized water (mass ratio = 1:9).

Comparing to the printing ink without PVA, the addition of minor PU into the printing ink would enhance the mechanical strength and decrease the mud cracks.

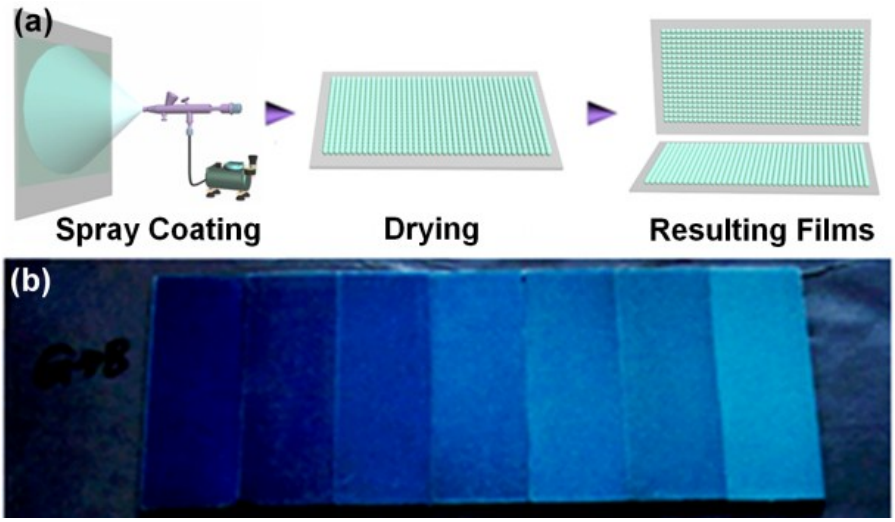

Figure S9. Spray printing of the colloidal printing ink. (a) Schematic illustration for the construction process of colloidal crystal films via spray painting. (b) Optical images of the resulting films prepared by alternately spraying the latex inks containing PS colloids of 195 and 215 nm.

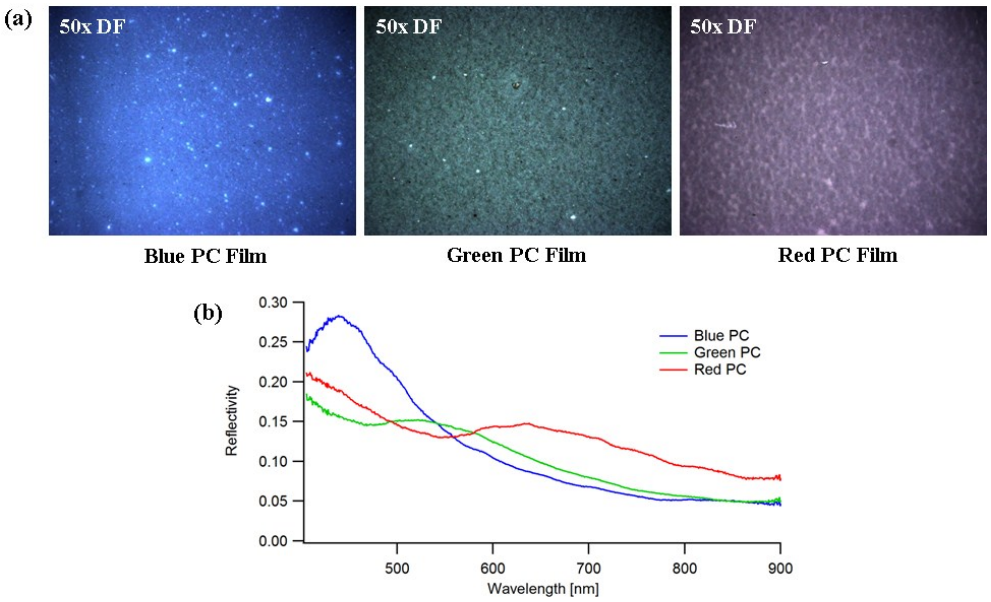

Figure S10. Optical performance of the resulting CPC films prepared by spray coating. (a) Optical images of the photonic crystal films constructed by alternately spraying the inks containing PS colloids of 195, 215 and 272 nm onto the glass substrate. (b) The reflection spectra of resulting sprayed photonic crystal films.

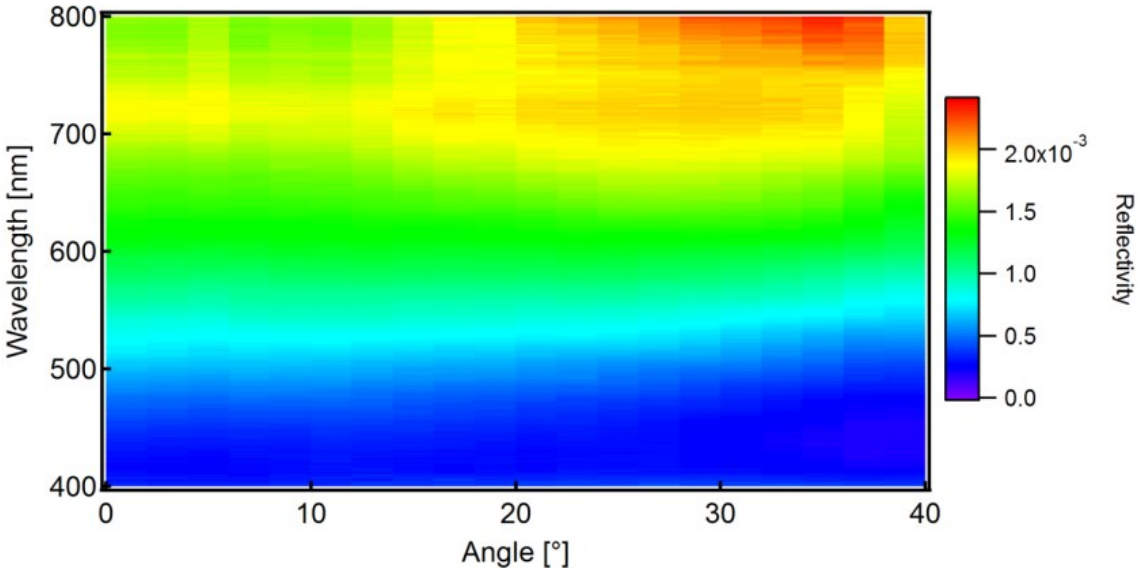

Figure S11. Goniometry measurement of the sprayed photonic crystal film. The CPC film was composed of 195 nm PS colloids.

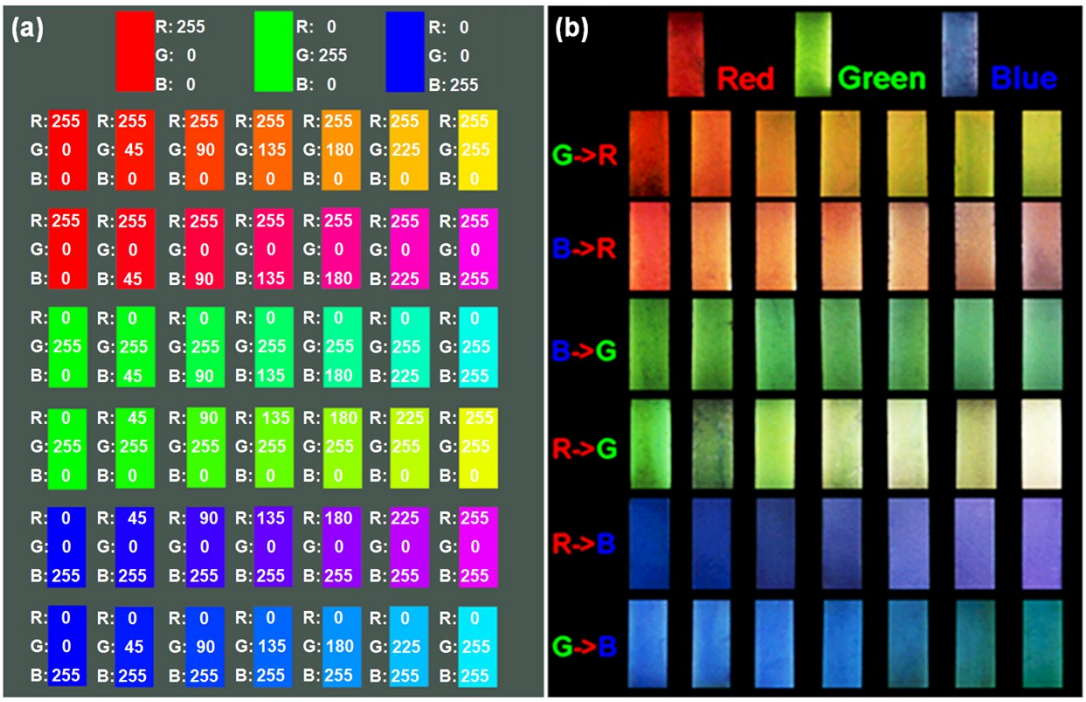

Figure S12. Construction of diverse optical films with different structural colors via spray coating. (a) Simulated colors generated by the palettes of Photoshop Software. (b) Colloidal crystal films with diverse colors attained by alternately spraying the inks containing PS colloids of 195, 215 and 272 nm onto the glass substrate. The printing ink herein contains 15 wt% PS colloids and 85 wt% deionzied water. The drying temperature and humidity were 25 ^{o}C and 40 %.

E. Real-time movies of the colloidal printing processes

1 Movie S1: The real-time assembly processes for the formation of coffee ring-like printing dots on a glass substrate.

2 Movie S2: The real-time assembly processes for the formation of dome-like printing dots on a glass substrate.

3 Movie S3: The real-time assembly processes for the formation of printing dots on the hydrophobic substrate.

4 Movie S4: The typical process for preparation of colloidal photonic crystals via bar coating.