Supporting Information

Polycrystalline SiO_2 Colloidal Crystal Film with Ultra-Narrow Reflections

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EXPERIMENTAL

Chemicals. Poly(ethylene glycol) diacrylate (PEGDA, Mn = 250 and 700) were purchased from Sigma-Aldrich. 2-hydroxy-2-methylpropiophenone (96%) was purchased from TCI Co. Ltd. Tetraethylorthosilicate (TEOS, 98%) and aqueous ammonium ($NH_3 \cdot H_2O$, 28%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ethanol (99.9%) was purchased from J&K. All chemicals were used directly as received without further treatment.

Synthesis of SiO_2/PEGDA photonic crystals film. Monodisperse silica particles were first synthesized by a modified Stöber method. The particles (30 μL) are well dispersed in ethanol (1100 μL) by sonication and then mixed with PEGDA (70 μL) to form a homogeneous dispersion. The mixture is heated to 90 °C for 2 hours to evaporate the ethanol content, which produces a liquid SiO_2/PEGDA precursor (~ 100 μL) in centrifuge tube. After being cooled down to room temperature, the precursor (30 μL) is sandwiched between two glass slides (pre-cooled to 0 °C) and left untouched for 20 minutes to form metastable SiO_2 colloidal crystals in PEGDA at 0 °C. Finally, the precursor is cured by UV light (365 nm, 4.8 mW/cm^2) for 1 min to fix the colloidal crystals and produce a photonic crystal film with ultra-narrow band gap. The recipe can be amplified 10-30 times, so that a circular photonic crystals film with larger size can be prepared.

Characterization. The particle size was determined by a JEOL JEM-2100 transmission electron microscope. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in dark-field mode. The reflection spectra were measured using an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection/back scattering probe, where both the incident and reflective angles are fixed at 0°. The micro-scale reflection spectra were measured by Idea Optics iMicro-A1 microscopic spectrometer with resolution down to 1 μm.

CALCULATION OF REFLECTION WAVELENGTH OF BRAGG SCATTERING

The reflection wavelength of Bragg scattering can be calculated from the diameter of silica particles (d = 165 nm), their volume fraction in polymer matrix (30%) and the refractive index of silica (1.46) and PEGDA (1.47). For colloidal crystals embedded in polymer matrix, the Bragg's Law can be expressed as Equation (1), where m is the order of diffraction, D is the center-to-center distance between nearest spheres, n_i and V_i are, respectively, the refractive index and volume fraction of each component, and ϕ is the angle between the incident light and the normal direction of the sample. According to Equation (2) and the known particle average diameter (165 nm), D is

calculated to be 223 nm. When the incident and reflective angle are fixed at 0°, the reflection wavelength is calculated to be 534 nm, which is close to the experimental results in Figure 1 and 4 (526-528 nm).

$$m\lambda = 2\sqrt{\frac{8}{3}}D\left(\sum_i \hat{a}_i^2 v_i^2 - \sin^2\theta\right)^{1/2} \quad (1)$$

$$(d/D)^3 \tilde{A}—74\% = 30\% \quad (2)$$

CALCULATION OF PHOTONIC BAND GAP WIDTH

The structure of the colloidal crystals is face-centered cubic (fcc). The refractive indices of the sphere (n) and the PEGDA matrix are 1.46 and 1.47, respectively. Since the volume fraction of the sphere is 30% according to the volume of silica particles and PEGDA, the ratio (a/d) between the lattice constant (a) and the particle's diameter (d) is about 1.91. The average diameter of the particles is determined to be 165 nm according to TEM images, and the calculated photonic band gap position at 0° is basically consistent with the measured value (526-528 nm) in Figure 1 and Figure 4.

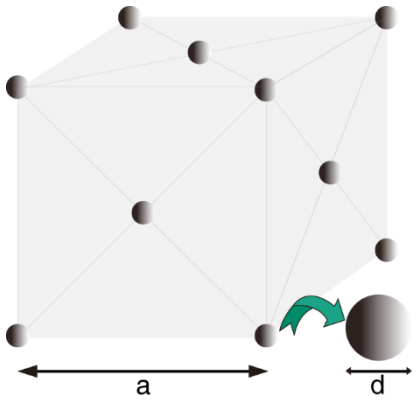

Figure S1. Face-centered cubic lattice (fcc).

By using the method of plane wave expansion, we calculate the band structure from the point *L* (111) to point *U* (1, 0.25, 0.25) of the Brillouin zone shown in Figure S2(a). Here, the number of the plane waves we used in the calculation is 16. From the results shown in Figure S2(a, b), the center wavelength of the photonic band gap is located around 527.5 nm and the band gap width is around 2 nm. Due to the principle of lowest energy, the most favorable lattice plane parallel to the surface of the film is the most compact plane, which is vertical to L (111) direction, as shown in Figure S1(b). Therefore, the missing photonic states inside the photonic band gap along the L (111) direction would result in a reflection peak at normal incidence, namely the calculated reflection at 527.5 nm with FWHM of 2 nm. It should be noted that these results are calculated based on an assumption that all the colloidal microcrystals have no defects and present the same orientation.

In practical measurement, the experimental FWHM value (~ 6 nm) is larger than the calculated peak width. This broadening of reflection might be caused by few defects within the microcrystals and slight difference in the crystal orientations.

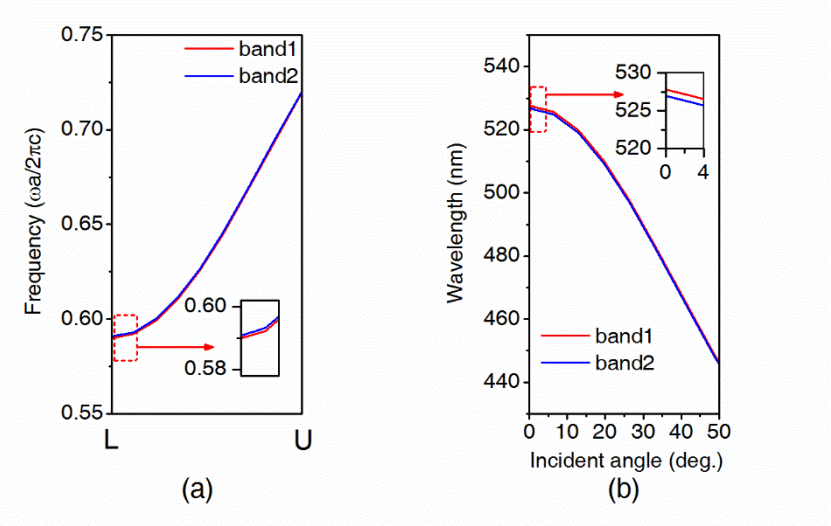

Figure S2. (a) Band structure from L to U. (b) Calculated reflectance peak of band 1 and band 2 at the border of Brillouin zone change as a function of incident angle.

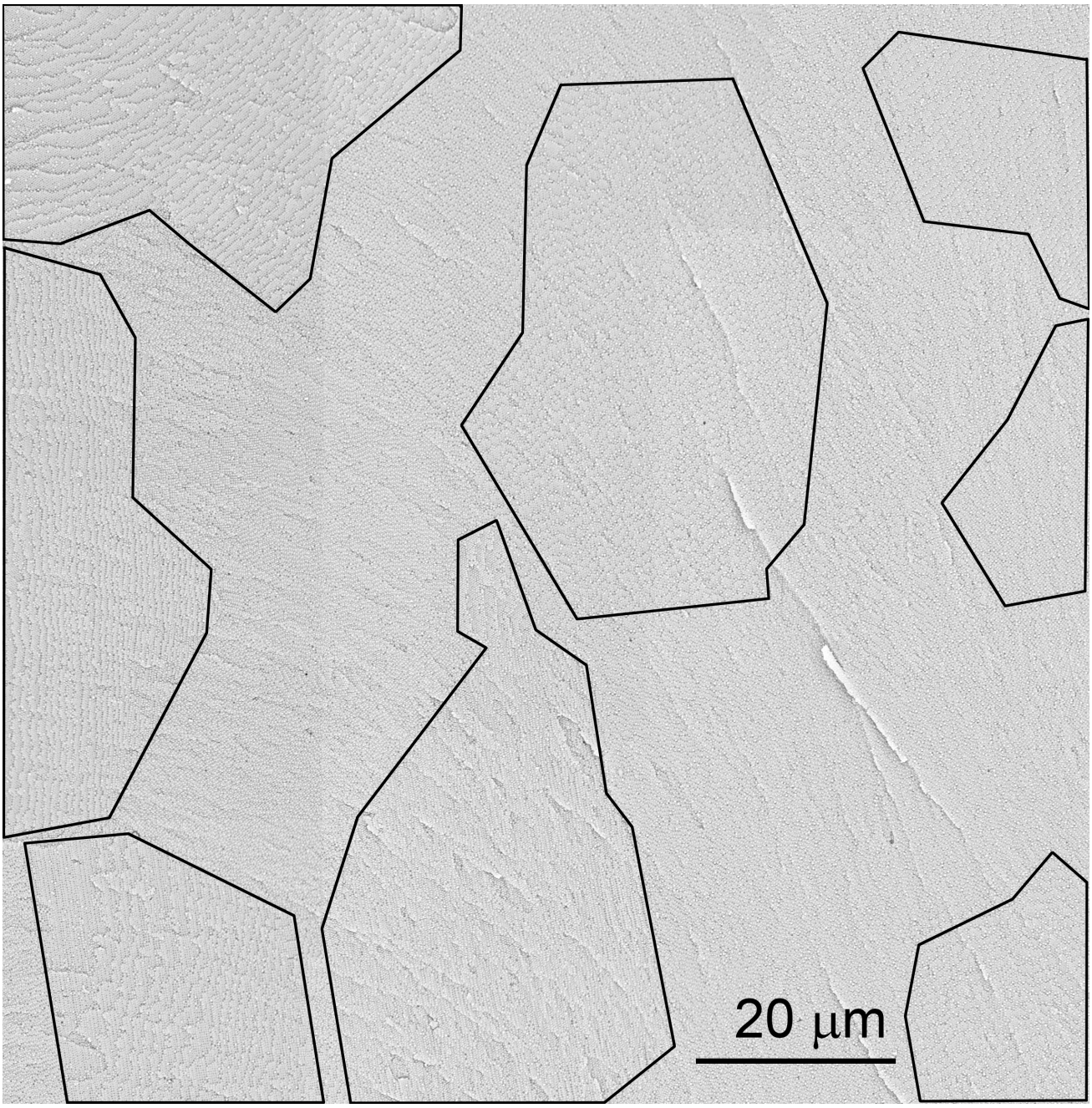

Figure S3. Cross-section SEM image of the polycrystalline colloidal crystal film. The crystalline regions are circled inside the black lines.

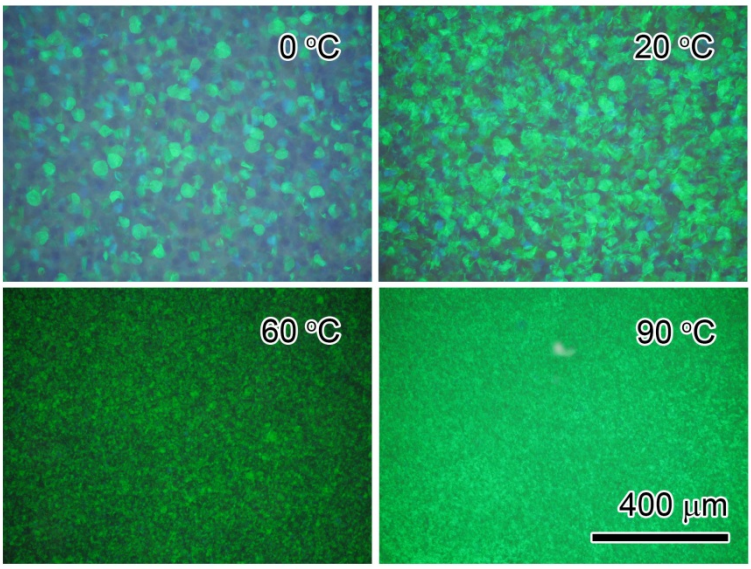

Figure S4. Optical microscope images of colloidal crystal films obtained at different temperatures.

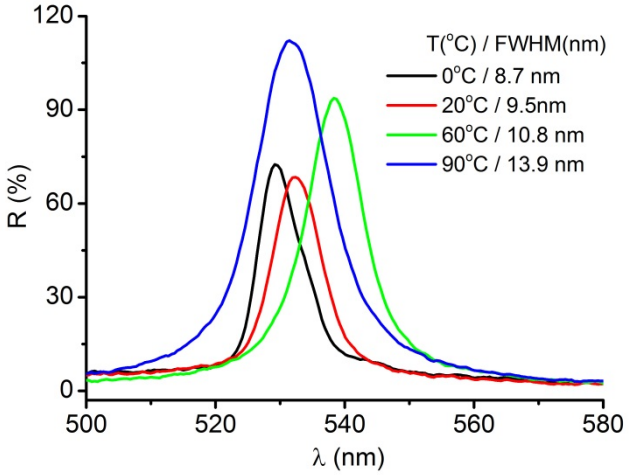

Figure S5. Reflection spectrum of colloidal crystal films obtained at different temperatures.

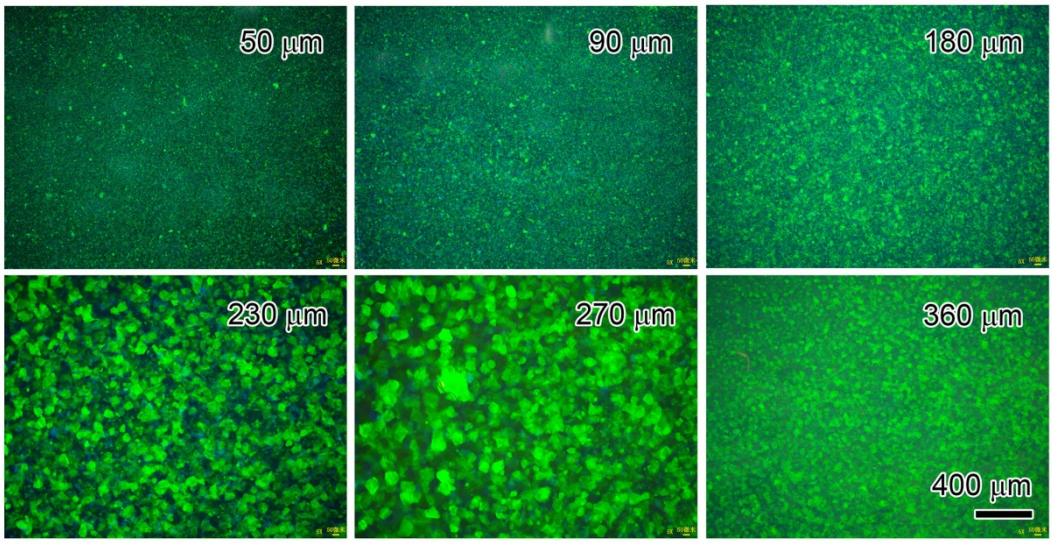

Figure S6. Optical microscope images of colloidal crystal films with different thicknesses.

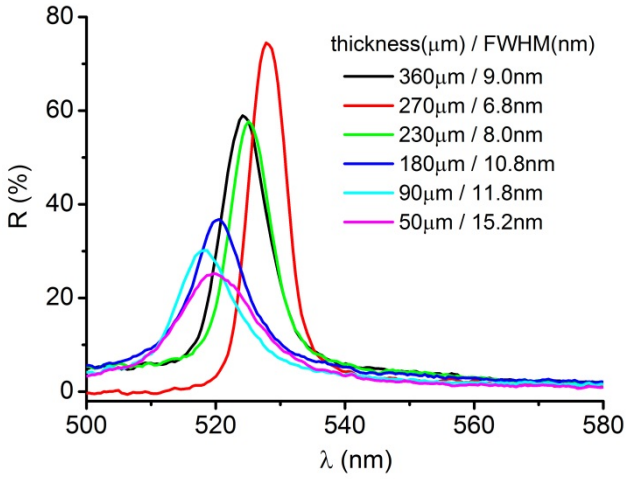

Figure S7. Reflection spectrum of colloidal crystal films with different thicknesses.