

Supporting information

Template-based Synthesis for Novel Polymeric Colloidal Photonic Crystals
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Materials and methods

Materials

Poly(ethylene glycol) diacrylate (PEGDA), ethylene glycol(EG), trimethylolpropane ethoxylate triacrylate (ETPTA), 2-hydroxy-2-methylpropiophenone, tetraethylorthosilicate (TEOS), ethanol(EtOH), cyclohexane(CYH), N-N dimethylformamide(DMF), hydrofluoric acid (HF) was purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Polyether-based thermoplastic polyurethane (TPU, Elastollan 1190A) was purchased from BASF Co. Ltd. polyhydroxyalkanoates (PHA) was purchased from Tianjin Guoyun Biology Co., Ltd. SYLGARDTm 184 Silicone Elastomer Kit was purchased from DOWSIL. All chemicals were used directly as received without further purification.

Fabrication of TPU inverse opal and PHA inverse opal

First, monodispersity SiO₂ particles were synthesized using an improved Stöber method. The SiO₂ particles (0.035 cm³) were dissolved via sonication in a mixture of ethylene glycol (65 μL) and ethanol (1.0 mL) to form a homogeneous solution. The solution was then transferred to an oven at 90°C and heated for 2 hours to remove the ethanol, resulting in a supersaturated SiO₂/EG colloidal solution with a total volume of 100 μL. This colloidal solution was spread onto pretreated

hydrophilic glass slides, with the thickness of the liquid film controlled at 38 μm intervals. After standing at room temperature for several minutes, the SiO_2 particles in the liquid film spontaneously precipitated to form a SiO_2/EG CPC. The liquid film was further heated at 90°C for 6 hours to evaporate the EG, resulting in a solid SiO_2 photonic crystal film on the glass substrate. Next, TPU powder (1.44 g) was dissolved in DMF (20 mL) at 100°C to prepare a TPU/DMF solution. The hot solution (20 mL) was immediately transferred into a cubic glass container measuring 10 cm \times 10 cm. The solid SiO_2 photonic crystal film on glass was immersed in this TPU/DMF solution for 30 minutes to allow the solution to fully penetrate the interstices of the SiO_2 particles via capillary action. Subsequently, the entire TPU/DMF solution was heated at 100°C for 2 hours to evaporate the DMF, resulting in a SiO_2 -TPU composite photonic crystal film. Thirdly, after peeling from the glass slide, the SiO_2 -TPU film was immersed in 8% mass fraction hydrofluoric acid aqueous solution for 60 minutes and rinsed three times with deionized water to produce collapsed inverse opal mesoporous TPU film structures. Inverse opal mesoporous PHA film was fabrication using the same method.

Fabrication of novel CPC materials

The prepared TPU template or PHA template was secured onto a glass slide using adhesive tape. Then, the precursor solution was uniformly coated onto the surface of the inverse opal material, allowing it to infiltrate into the pores through capillary. Depending on the characteristics of the precursor solution, an appropriate curing method was selected. After the precursor solidifies, the composite material was immersed in a DMF solution to remove the template, resulting in the fabrication of a novel CPC material.

Characterizations

The TPU template and the novel CPC materials were characterized by Zeiss Gemini 450 and Phenom G2 Pro scanning electron microscope (SEM). The reflection spectra of CPC films were measured by an Idea Optics FX2000 spectrometer coupled with a six around-one reflection probe. The fourier transform infrared spectrometer was measured by Thermo Scientific Nicolet iS50 in ATR mode.

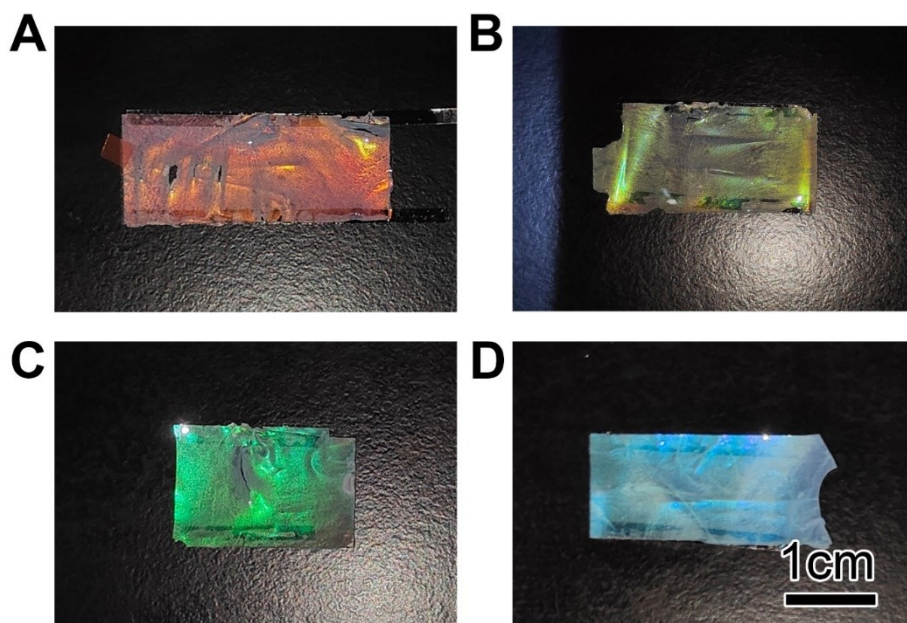


Fig. S1. Digital photo of 60%PE ET-PE-based CPC with different colors. (A) Red. (B) Yellow. (C) Green. (D) Blue.



Fig. S2. Digital photos of ET-PE-based CPCs' structural microcrystals dispersed in water.

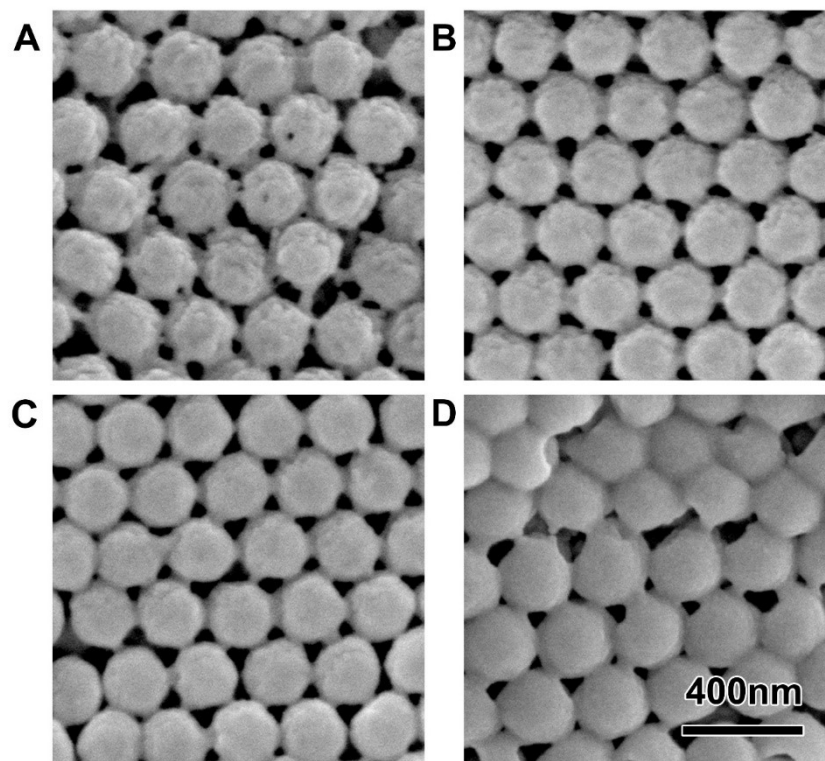


Fig. S3. SEM of ET-PE-based CPC with different PE proportions. (A) 20%PE. (B) 40%PE. (C) 60%PE. (D) 80%PE.

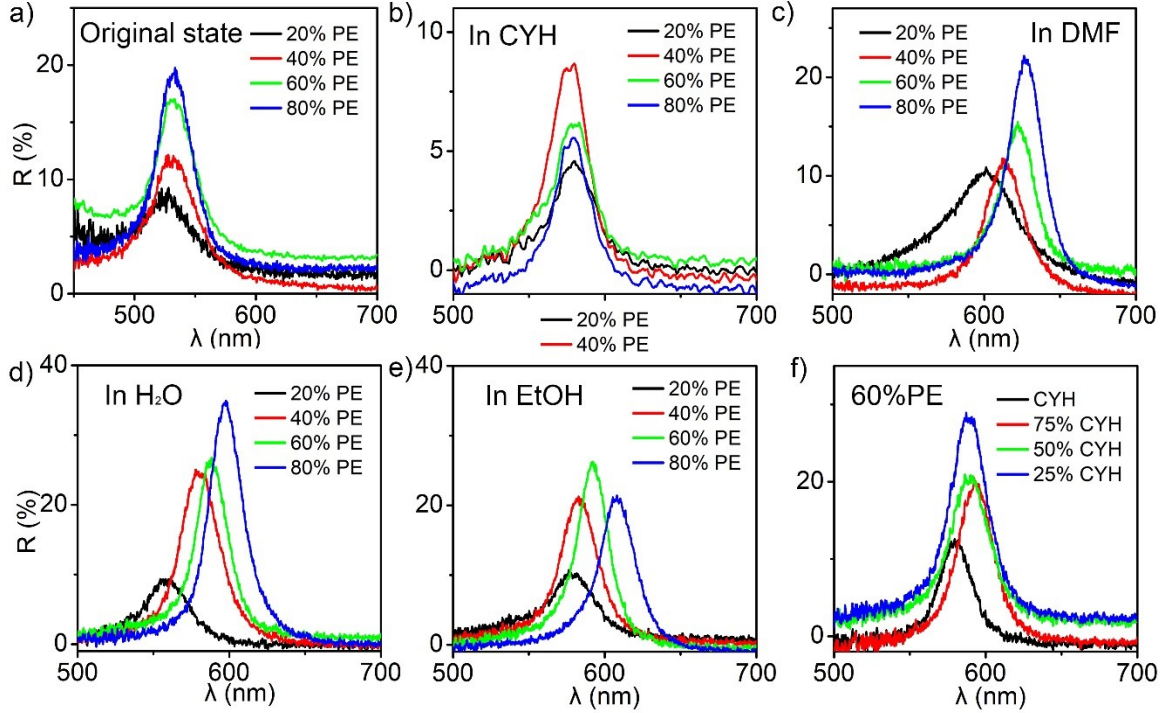


Fig. S4. Reflection spectra of ET-PE CPCs with different proportions in different state. (A)Original state. (B) Soaked in CYH. (C) Soaked in DMF. (D) Soaked in H₂O. (E) Soaked in EtOH. (F) 60% PE ET-PE CPCs soaked in mixture solution of CYH and EtOH.

When ET-PE PC was soaked in CYH and DMF, the reflection wavelengths were 578nm and 620nm, respectively. Given that the refractive index of both CYH and DMF is 1.43, according to the Bragg formula, the reflection wavelengths should be the same. However, the actual situation was quite different. To understand this discrepancy, we examined the structural characteristics of the materials involved. In previous reports, polymers with different crosslinking degree exhibit varying expansion rates in polar solvents. Based on the structural characteristics of PEGDA and ETPTA, we hypothesized that the higher the ETPTA content in the film, the higher the crosslinking degree, and consequently, the lower the expansion rate in polar solvents. By exposing ET-PE films with different compositions to solvents of varying polarities, we observed that in polar solvents, the higher the degree of crosslinking, the lower the expansion rate, while non-polar solvents did not significantly alter the material, as demonstrated in Movie S1. Therefore, we concluded that the

material swelled in polar solvents, altering its lattice constant and causing the reflection wavelength in DMF to redshift relative to that in CYH.

By adjusting the composition of the building blocks material, CPCs materials with different expansion rates in polar solvents could be prepared. Using the same inverse opal material as a template, four ET-PE-based CPCs materials were prepared with precursor solutions of PEGDA and ETPTA, containing 20%, 40%, 60%, and 80% PEGDA, respectively, as shown in the Fig.S3. Since PEGDA and ETPTA have the same refractive index of 1.47, the reflection peaks of the four CPCs were all around 530nm when in dry. When the four materials were soaked in CYH, which could not cause the building blocks to swell, and since the refractive index of CYH is higher than that of air, the reflection wavelength of the four materials redshifted from 530nm to 578nm with the increase of PEGDA content. Notably, compared to the reflection wavelength of the four materials soaked in CYH (578nm), the materials soaked in DMF, which has a refractive index almost the same as CYH, exhibited a significant redshift in their reflection peaks with the increase of PEGDA content in the building blocks. Specifically, the reflection peaks of the CPCs with 20%, 40%, 60%, and 80% PEGDA content were 599nm, 613nm, 622nm, and 627nm, respectively. Similarly, when these materials were soaked in ethanol and water, the reflection wavelengths underwent redshift with the increase of PEGDA content. As an example, an ET-PE-based CPCs material with 60% PEGDA content was soaked in a mixed solvent of CYH and ethanol. Although the refractive index of CYH (1.43) was higher than that of ethanol (1.36), the reflection wavelength still showed a redshift upon the addition of ethanol, indicating that the addition of ethanol altered the lattice constant of the material. Therefore, the novel CPCs material can perfectly inherit the properties of polymer materials, providing a novel avenue for the subsequent preparation of functional CPCs materials.

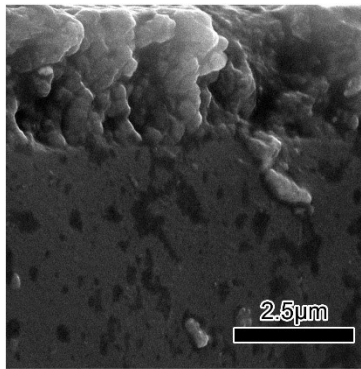


Fig.S5. Cross-sectional SEM image of PDMS-based CPCs.

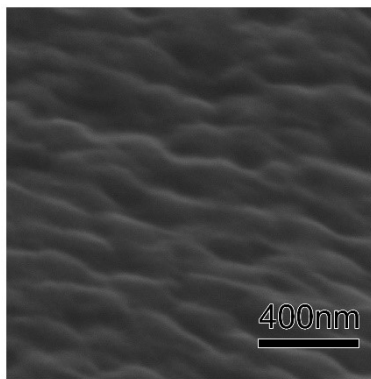


Fig. S6. Top-view SEM image of PDMS-based CPCs in stretching state.