Supporting information

Controllable Preparation and Orientation-Dependent Retroreflective Structural Color Properties of Anisotropic Colloidal Photonic Crystals

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Materials and methods

Materials: Ethyl orthosilicate (TEOS, 98.0%), ammonia (26%), anhydrous ethanol, N,N-dimethylformamide (DMF, 99.5%), and hydrofluoric acid (HF) were obtained from National Pharmaceutical Chemistry Trial Co. Ethylene glycol (EG, 99%), trimethylolpropionic acid triacrylate (ETPTA, 85%), polyethylene glycol diacrylate (PEGDA), and 2-hydroxy-2-methylpropiophenone (97%) were purchased from Aladdin Chemical Co. Polyether-basedthermoplastic polyurethane (TPU, Elastollan 1190A) was obtained from BASF Co. Ltd. All chemicals were employed directly as received, without further purification.

Synthesis of SiO_2 Particles: SiO_2 particles with controlled dimensions were synthesized via a seed-mediated growth approach. Initially, TEOS (5.55mL) was hydrolyzed in an aqueous arginine solution (0.09 g in 87 mL of water) at 70 °C for 24 hours. The resulting hydrolyzed solution was cooled to room temperature and used directly as the seed solution. In a typical growth procedure, seed solution (200 μL) was mixed with ethanol (200 mL), water (14 mL), and ammonia solution (8 mL). TEOS (6 mL) was then introduced into the mixture at a constant injection rate of 10 $mL \cdot h^{-1}$. After 10 hours of reaction, SiO_2 particles with a diameter of 160 nm were obtained. Under similar reaction conditions, increasing the amount of TEOS to 14 mL yielded SiO2 particles with a diameter of 215 nm. The synthesized SiO_2 particles were subsequently washed three times with ethanol via alternating cycles of centrifugation and redispersion, and finally stored as a dispersion in ethanol.

Preparation of TPU Inverse Opal Temlapte： A homogeneous solution was prepared by dispersing SiO_2 particles (0.030 cm^3) in a mixture of ethylene glycol (EG, 70 μL) and ethanol (1.0 mL) via sonication. The solution was heated at 90°C for 2 h to evaporate ethanol, yielding a 100 μL supersaturated SiO_2/EG colloidal solution. This solution was spread onto a pretreated hydrophilic glass slide using a blading method, controlling the liquid film thickness at 40 μm. After room-temperature settling for several minutes, SiO_2 particles self-assembled into a liquid colloidal photonic crystal (PC) film. The film was then heated at 90°C for 6 h to remove EG, resulting in a solid SiO_2 PC film on the glass substrate. Subsequently, a TPU/DMF solution was prepared by dissolving 5.5 g of TPU in 20 mL of DMF at 85 °C. The hot solution (20 mL) was immediately transferred into a cubic glass container with a base dimension of 10 cm × 10 cm. The solid SiO_2 PC film on the glass slide was immersed into the solution for 10 minutes to allow complete capillary infiltration of the solution into the interstitial voids of the SiO_2 particles. The entire system was then heated at 85 °C for 30 minutes to evaporate the DMF, yielding a SiO_2–TPU composite PC film. The SiO_2-TPU composite PC films were peeled off from the glass slide and then immersed in a 5% (mass fraction) hydrofluoric acid (HF) aqueous solution for 2 hours to selectively etch away the SiO_2 template. After etching, the films were rinsed repeatedly with deionized water for 3 times, and finally, reverse opal-structured films were obtained.

Fabrication of ACPCs: The polymer precursor solution was prepared as follows: 150 μL of PEGDA, 150 μL of ETPTA, and 10 μL of 2-hydroxy-2-methylpropiophenone were thoroughly mixed using a homogenizer. The inverse opal template was fixed to a rubber substrate with adhesive tape, mounted onto a tensile testing device, and subjected to uniaxial strains of 30%, via precision-controlled displacement. The precursor solution was then injected onto the strained template, covered with a glass slide, and cured by UV photoinitiation. The resulting composites were immersed in DMF to completely dissolve the TPU template, yielding ACPCs. Building on the prior work where a 30% strain was applied along the X-axis, additional secondary strains of 20% and 40% were imposed along the Y-axis. Following the same precursor injection and photopolymerization protocol, ACPCs with oblate morphologies were successfully fabricated.

Fabrication of Anti-counterfeit Labels Based on ACPCs: Using a conventional inverse opal template (160 nm SiO_2 particles) as the background layer and a patterned inverse opal template (215 nm SiO_2 particles) as the pattern layer, the two templates were separately bonded onto a rubber substrate and mounted in a stretching device. A polymer precursor solution was injected into the gap between the templates, followed by 20% uniaxial tensile strain applied to the pattern layer. After polymerization was induced and the TPU template was removed, a synchronously stretched composite anti-counterfeiting material with both background and pattern layers was obtained.

Characterizations: The assembly of polymer particles in photonic crystals was characterized using a Hitachi S4800 scanning electron microscope (SEM). The reflectance spectra of the ACPCs were measured by an Ocean Optics Maya 2000 Pro spectrometer and six peripheral 1 reflectance probes. The angles of incidence and reflection were fixed at 0°. The fourier transform infrared spectrometer was measured by Thermo Scientific Nicolet iS50 in ATR mode

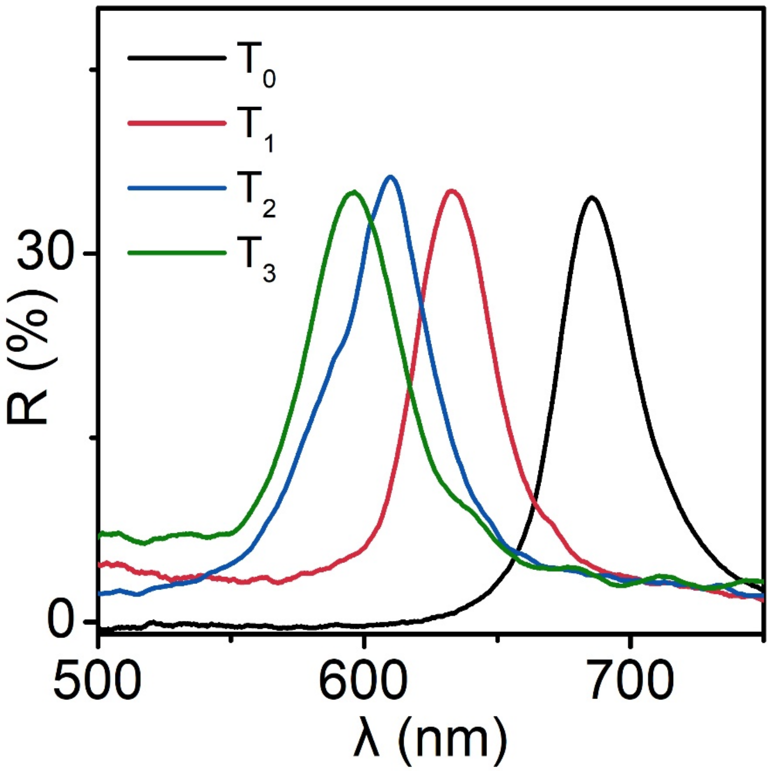

Fig. S1. Reflection spectra of T_0-T_3.

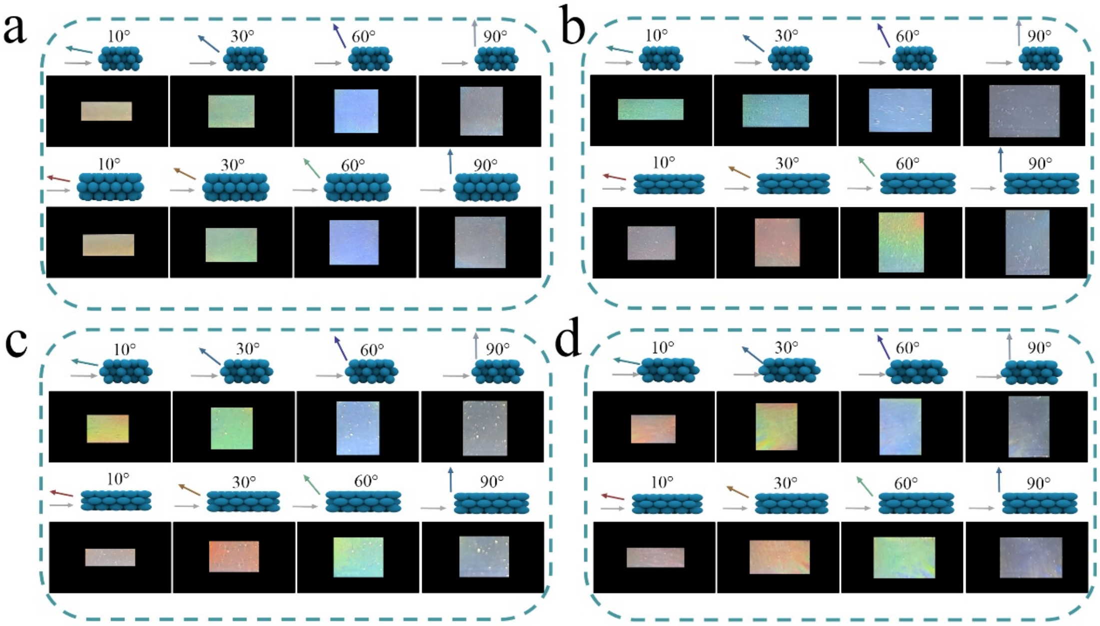

Fig. S2. The angular-dependence retroreflective structural colors of T_0-T_3 along minor axis and major axis. a) T_0, b) T_1, c) T_2, d) T_3.

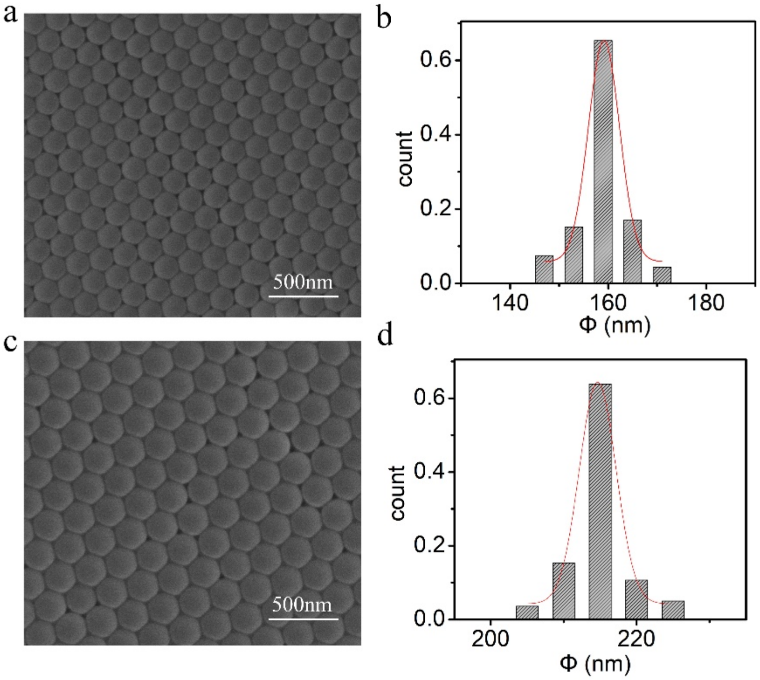

Fig. S3. a) SEM images, and size distribution of SiO_2 particles (160 nm), b) SEM images, and size distribution of SiO_2 particles (215 nm)

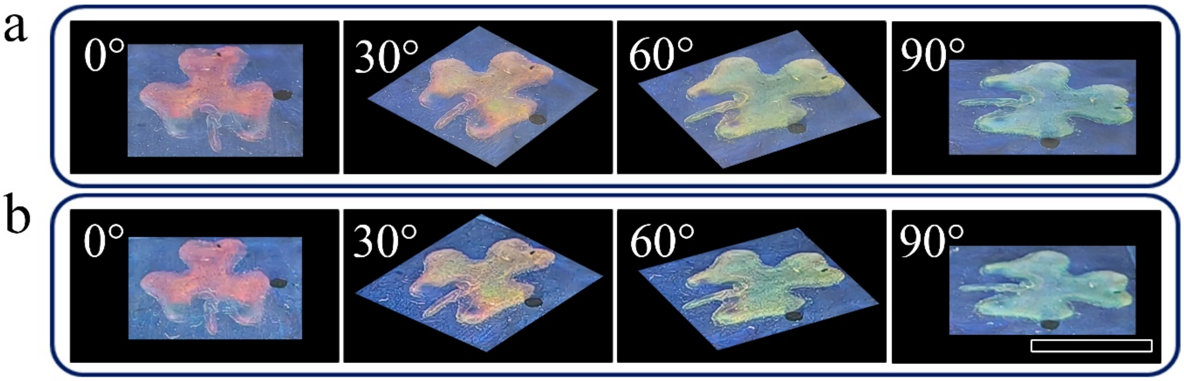

Fig. S4. a) Initial state of the anti-counterfeiting label's retroreflective photos， b) Anti-counterfeiting label's retroreflective photos after immersion in water, ethanol, and DMF for two days.