

SUPPORTING INFORMATION

Optofluidic Assembly of Colloidal Photonic Crystals with Controlled Sizes, Shapes and Structures**

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S1. Colloidal silica particles dispersed in ETPTA resin.

Silica particles in the refractive index matching ETPTA medium with high polarity spontaneously organize into an ordered phase at low concentrations on account of a strong repulsive potential relative to a diminishing van der Waals attraction. Indeed, as shown in Figure S1, silica particles dispersed in ETPTA resin diffracted light and displayed iridescent colours at concentrations as low as $\phi = 0.1$. The main reflection wavelength λ depends on the particle radius a and volume fraction ϕ , and can be estimated by Bragg's equation for a normal incident beam onto the (111) plane of an FCC structure:

$$\lambda = 2dn_{eff} = \left(\frac{\pi}{3\sqrt{2}\phi}\right)^{1/3} \left(\frac{8}{3}\right)^{1/2} 2a(n_p^2\phi + n_m^2(1-\phi))^{1/2} \quad (1)$$

which assumes a constant interparticle distance for all nearest neighbors at a given volume fraction.

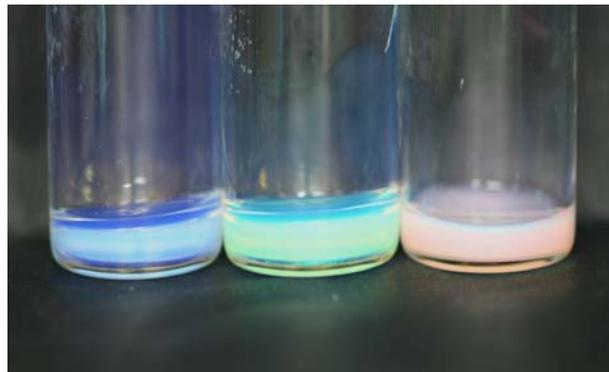


Figure S1| Iridescent colors of silica-in-ETPTA suspensions at different particle concentrations and sizes. Blue, green and red suspensions are composed of 145 nm silica particles at $\phi = 0.33$, 152 nm silica particles at $\phi = 0.25$ and 190 nm silica particles at $\phi = 0.25$, respectively.

S2. Effect of viscosity on the shape relaxation

During shear-induced emulsification, the silica suspension was elongated and broken into small droplets. The emulsion drops were elongated initially but relaxed to a spherical shape if

the particle concentration was not too high to immobilize the interface. The time scale of the relaxation from the deformed elongated shape to a spherical shape is given by $t = \eta d_d / \gamma_{ow}$, where η is the viscosity of the suspension, γ_{ow} is the interfacial tension, and d_d is the diameter of the drop in spherical shape. Therefore, the relaxation time scale will be strongly dependent on the particle concentration, which has a dramatic effect on the suspension viscosity (see Figure S2a). For example, when ϕ is less than 0.33, the relaxation time scale to a spherical shape is less than 1 second, as shown in Figure S2b. However, when ϕ is as high as 0.5, the suspension viscosity increases abruptly and three-dimensional jamming of the colloidal particles occurs. In this case, shown in Figure S2c and 2Sd, the colloidal crystals remained non-spherical with compactly packed colloidal particles. These findings indicate that at high colloidal particle concentrations, the deformed silica-in-ETPTA drops formed during shear-induced emulsification cannot relax to a spherical shape after the shear field is removed.

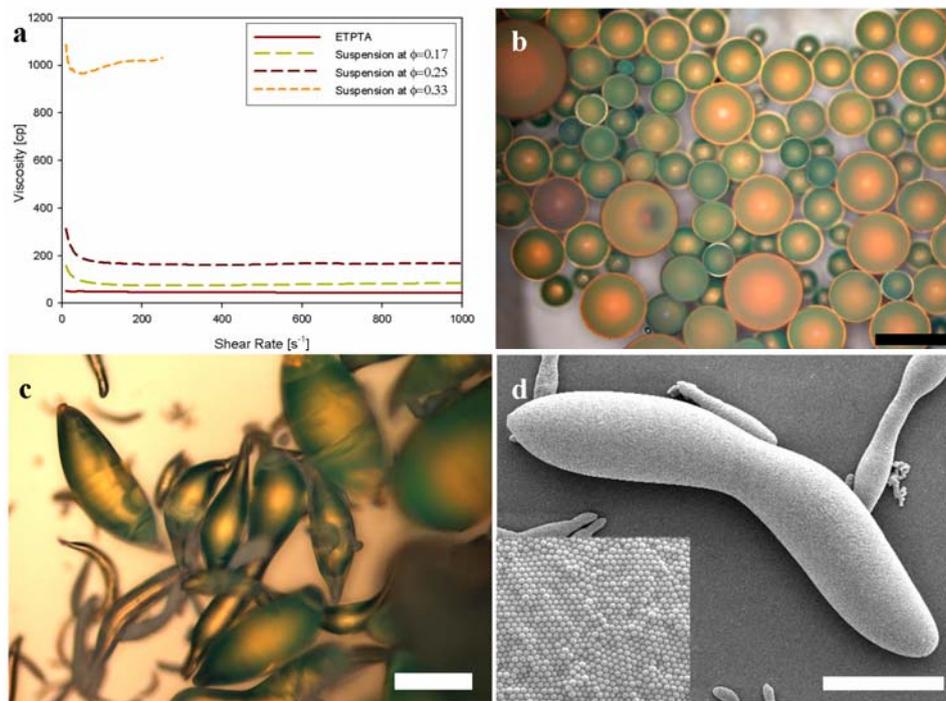


Figure S2| Effect of suspension viscosity for various particle volume fractions. a, Viscosity data measured at 27 °C for 200 nm silica particles suspensions at $\phi = 0.33$, $\phi = 0.25$, $\phi = 0.17$ and $\phi = 0$ in ETPTA. **b,** Optical microscope image of spherical photonic balls composed of 165 nm silica particles embedded in ETPTA at $\phi = 0.25$. **c,** Optical microscope image and **d,** SEM image of non-spherical photonic structures composed of 200 nm silica particles at $\phi = 0.5$ in ETPTA. Scale bars are 200 μm in **b** and **c**, and 20 μm in **d**.

S3. Microfluidic Emulsification

Still shots at three different positions show that the microfluidic device can generate highly monodisperse ETPTA droplets in aqueous flow stream. Each ETPTA drop contains a certain number of colloidal silica spheres.

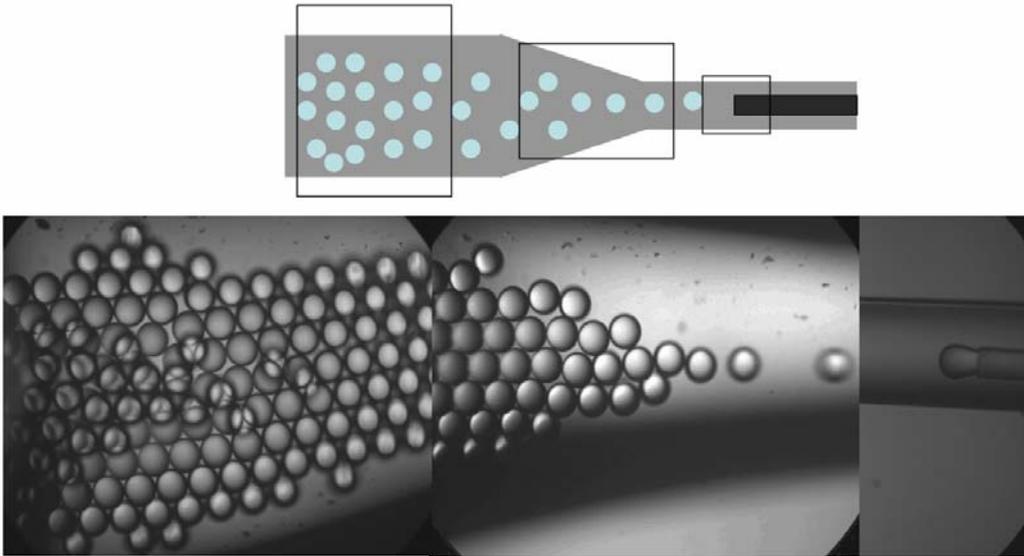


Figure S3| Still shots of microfluidic emulsification.

S4. Capillary-flow driven assembly

Silica-in-ETPTA composites with other shapes can be readily fabricated using different templates. For example, we created composite photonic crystal films by inserting the suspension via capillary forces into the gap between two parallel plane glasses separated at a distance of $d = 50 \text{ }\mu\text{m}$. Because of the high viscosity of the suspension, this infiltration proceeded slowly (~ 1 hour) and the velocity gradient ($\sim \gamma_{AO} / \eta L$) was extremely small across the gap. Here, γ_{AO} is the surface tension of the air-ETPTA interface and L is the length of the gap in the flow direction. Also, the capillary-induced flow reached a steady state laminar flow from a disturbed state at a time scale of $t \sim \rho d^2 / \eta$, which is extremely small (on the order of 10^{-9} sec). Under these circumstances, the capillary flow will not disturb the ordered state of colloidal silica particles formed in the ETPTA resin. As shown in Figure S4, the solidified films display uniform reflection colours, indicating that they are high-quality photonic crystals with no cracks. Using the same approach, we created photonic crystals with various shapes by inducing capillary-force-driven flow through microcapillaries with different geometries. We prepared, for example, striped cylindrical photonic crystals by sequential infiltration of different-coloured silica suspensions into glass capillary tubes. After solidification under UV exposure followed by removal of the template glass tubes, freestanding cylinders with striped reflection colours were produced, as shown in Figure S5.

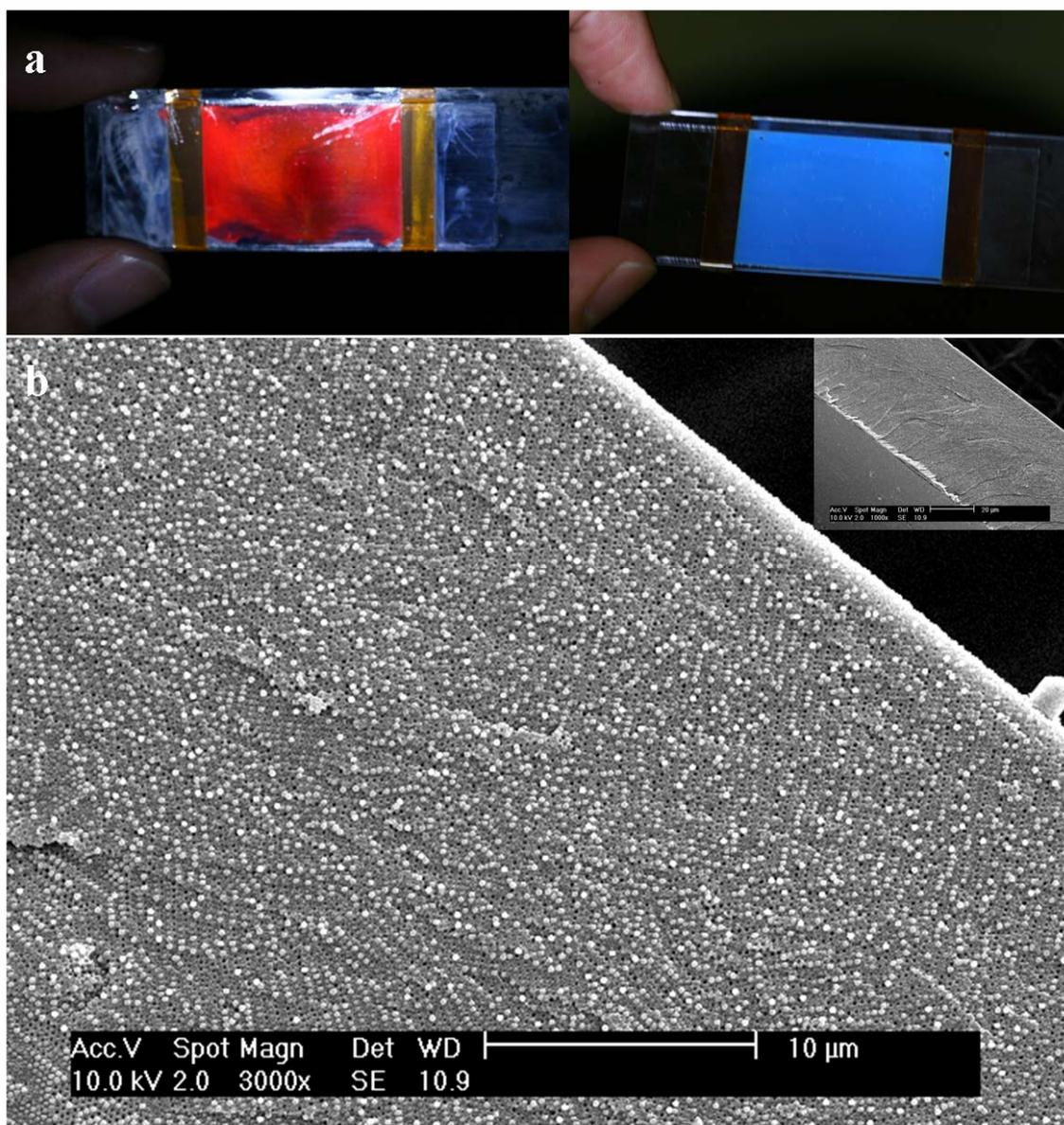


Figure S4| Photonic films. **a**, Composite colloidal crystal films with red and blue colors and **b**, cross-sectional image of red-colored film. Inset of **b** showed a low magnification image of the cross-section. The red and blue films are composed of 195 nm and 145 nm silica particles at $\phi = 0.33$.

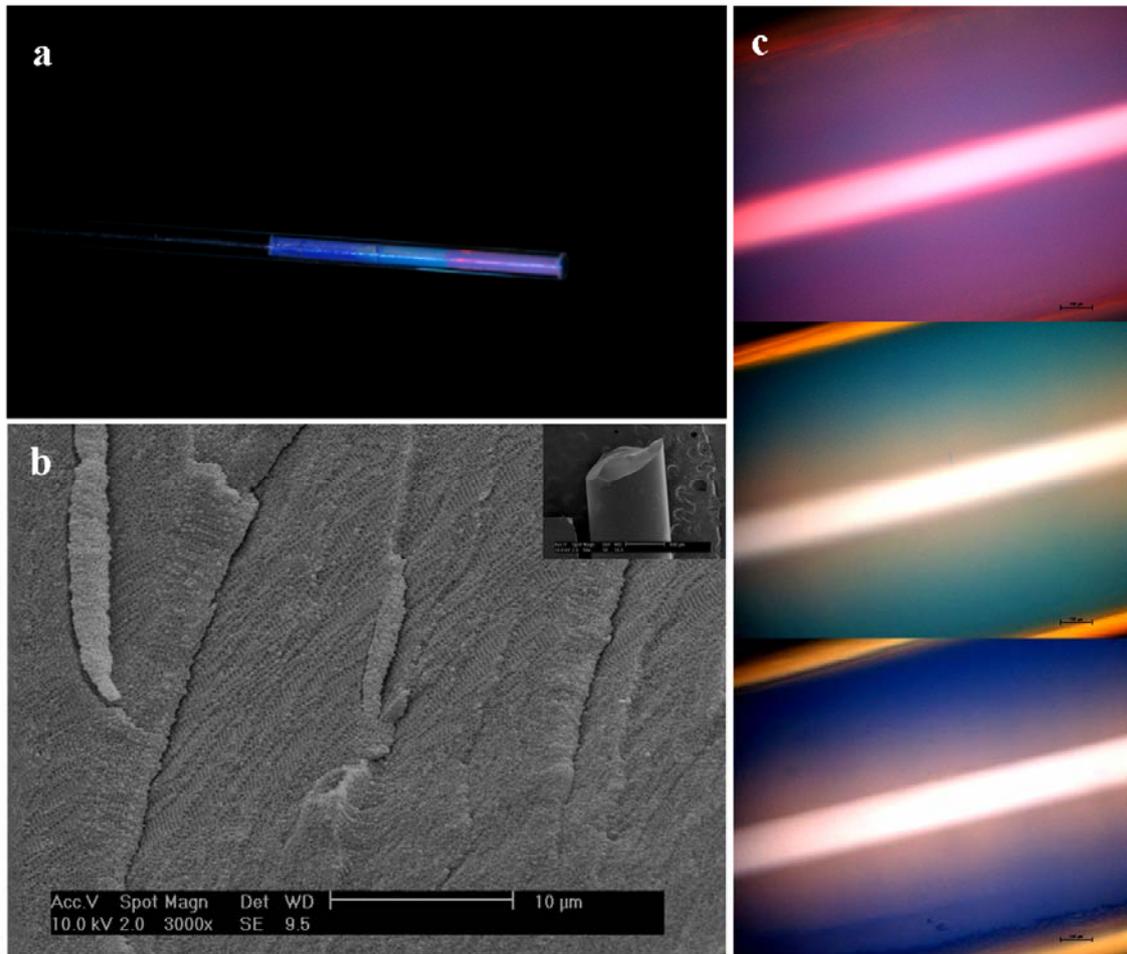


Figure S5| Photonic cylinders. **a**, photonic cylinders with striped red, green and blue reflection colors with 1.1 mm in diameter. **b**, Cross-sectional SEM images of fractured red cylinder. Inset of **b** showed a low magnification image of fractured cylinder. **c**, Optical microscope images of corresponding red, green and blue stripes. Blue, green and red colors originate from 145 nm silica particles at $\phi = 0.33$, 152 nm silica particles at $\phi = 0.25$ and 195 nm silica particles at $\phi = 0.33$, respectively.