Electronic Supplementary Material (ESI) for Lab on a Chip.
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Stop Flow Lithography in Perfluoropolyether (PFPE) Microfluidic Channels

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I. Optical properties of SIFEL devices

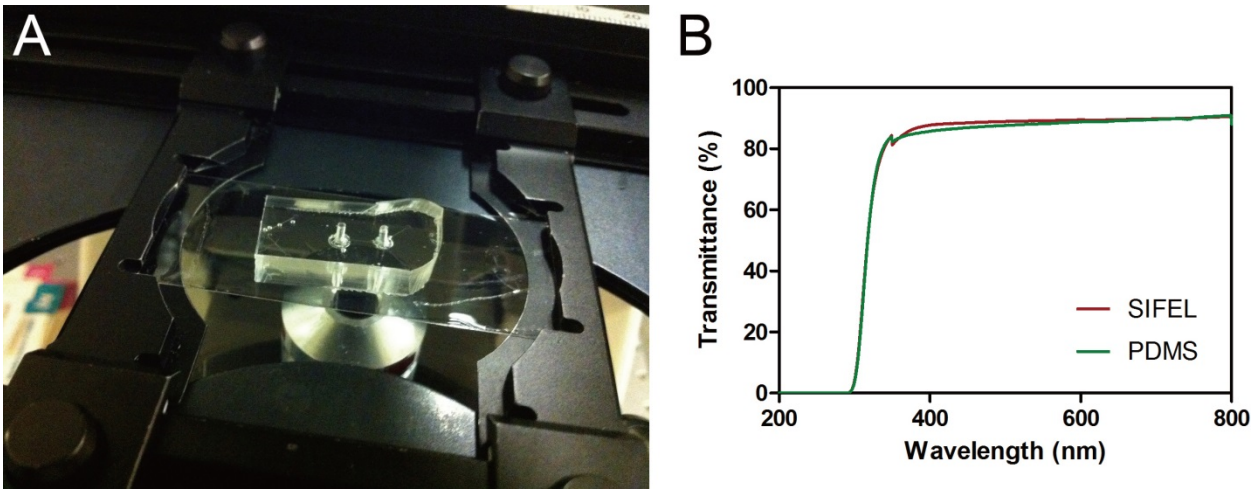

Figure S1. The optical properties of SIFEL devices. (A) A bright field image of a SIFEL device mounted on an inverted microscope. The device is optically transparent as mentioned in the Reference S1. (B) The comparison of transmittances measured from SIFEL and PDMS devices. The transmittance of SIFEL devices is almost identical to the one of PDMS devices. The transmittances for both devices were measured using UV-vis spectroscopy. We additionally note that the transmittance of the SIFEL device was not changed after 10 minutes of UV exposure.

II. Elastic Modulus of PFPE

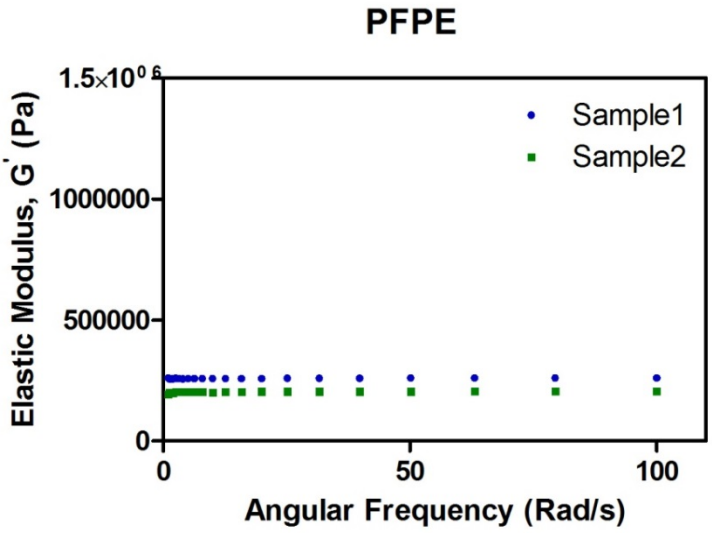

Figure S2. The elastic modulus of PFPE was measured by a stress-controlled rheometer. After cylindrical PFPE elastomer samples with 20 mm diameter were placed in rheometer, the elastic modulus was measured through frequency sweep from 0 to 100 rad/s. The average of measured elastic modulus for two PFPE samples was 0.25 MPa**.** As the elastic modulus of PDMS is 1 MPa[2], PFPE has 4 times lower elastic modulus than PDMS.

III. Maximum particle synthesis throughput of PFPE-based SFL

The SFL process requires a stop time for the channel relaxation of the elastic devices. As mentioned in the main text, PFPE channels need 4 times longer relaxation time than PDMS channels. This leads to 4 times increase of the stop time in PFPE-based SFL, reducing the particle production rates. The maximum particle synthesis throughput for PDMS-based SFL was estimated in Reference S3. Based on the operation times of PDMS-based SFL for this synthesis condition, we estimated the maximum particle synthesis throughput of PFPE-based SFL in table S1.

Table S1. Comparison for the maximum particle synthesis throughput of each type of SFL

Process	Stop	Polymerization	Flow	Cycle Time	Throughput (Particles/min)
PDMS-based SFL [Ref. S3]	~ 20 ms	~ 50 ms	~ 110 ms	~ 180 ms	~ 10^7
PFPE-based SFL	~ 80 ms	~ 50 ms	~ 110 ms	~ 240 ms	~ 7.5×10^6

IV. Solvent effects on fluorescent intensity of UCNs

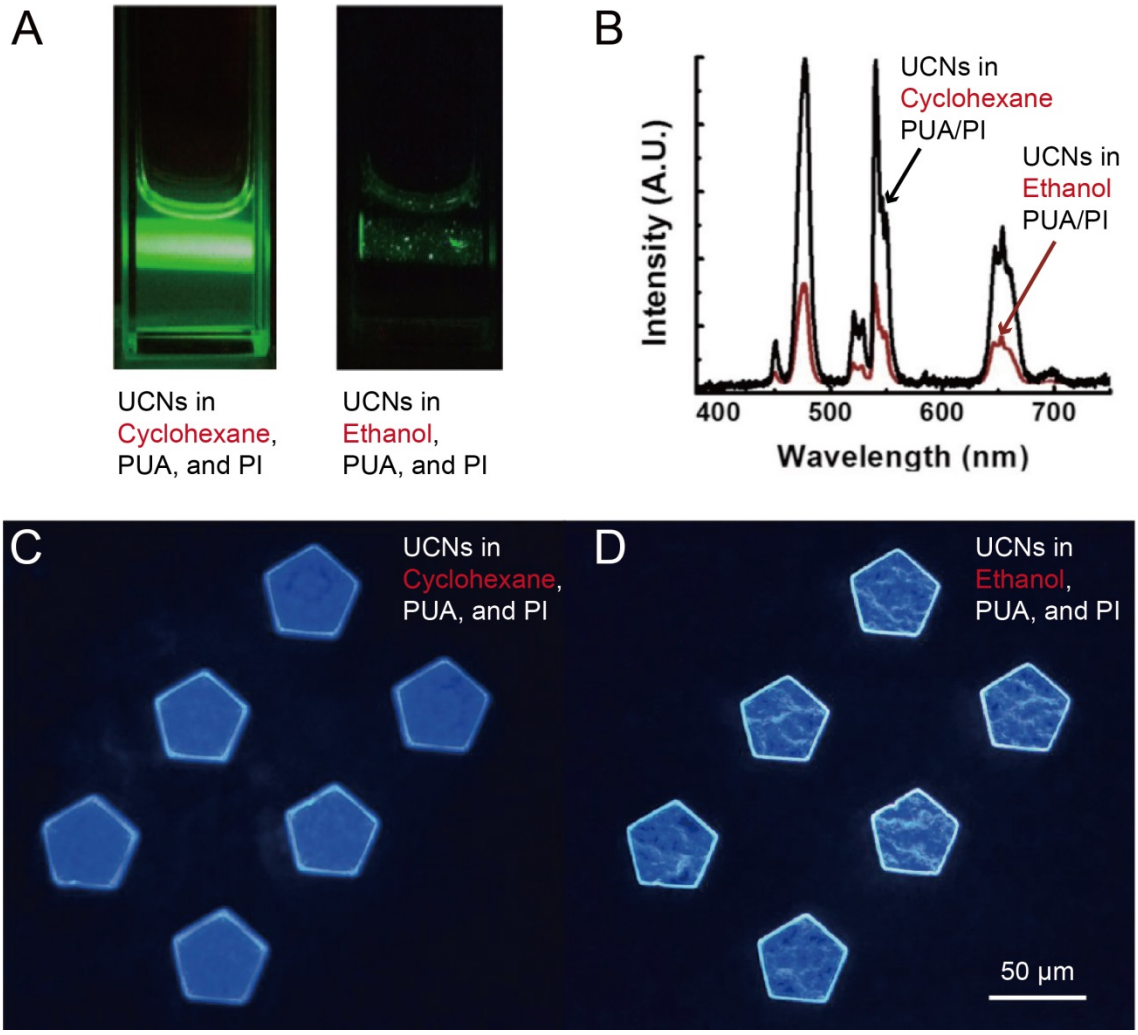

Figure S3. (A-B) The upconversion nanocrystals (UCNs) in a nonpolar solvent, cyclohexane are homogeneously mixed with the precursor solution of polyurethane acrylate (PUA) and photoinitiator (PI). On the contrary, the UCNs in a polar solvent, ethanol are aggregated in the mixture with PUA precursor solution. This aggregation leads to the significant reduction of the fluorescent intensity of UCNs. (C-D) Luminescence images of photopolymerized particles on a glass slide. The fluorescent signal homogeneity of the particles reflects the stability of the UCNs dispersion in the precursor solution. The composition of the precursor solution is 50% (v/v) PUA, 40% (v/v) UCNs in a solvent, and 10% (v/v) PI.

V. Critical height of the bottom PFPE coating

Stop flow lithography consists of three steps including stop, photopolymerization, and flow. The typical time scales in each step are 500 ms for stopping flow, 50 ms for photopolymerization, and 1 s for flow, respectively. The oxygen concentration in the PFPE layer will be consumed in the short period of the photopolymerization. However, we can assume that the consumed oxygen concentration in the PFPE layer is refilled from the air or precursor solution in the relatively long period of the other steps. With this assumption, the oxygen concentration in the PFPE layer is considered to be the equilibrium concentration at the starting of the photopolymerization step. For the photopolymerization step, we will treat the oxygen diffusion in the PFPE layer as the 1D time-dependent diffusion in a film. Then, the characteristic length scale of oxygen diffusion in the PFPE layer can be estimated by the following equation,

$$\sqrt{D_{PFPE} t_{photopolymerization}} \sim \sqrt{5.73\times10^{-9}(m^2/s)\times 0.05(s)} = 17\mu m \sim \delta$$

Where D_{PFPE} is the oxygen diffusivity in PFPE, $t_{photopolymerization}$ is the time scale for the photopolymerization step, and δ is the characteristic length scale of oxygen diffusion. The D_{PFPE} is estimated from the oxygen diffusivity (7.88×10^{-9} m^2/s) in PDMS[4], assuming that the diffusivity is proportional to the oxygen permeability.

The critical oxygen concentration required to generate oxygen lubrication layers is much smaller than the equilibrium oxygen concentration in the film[5]. Also, oxygen is assumed to flow freely in the film because the diffusivity of oxygen in PFPE is much larger than the diffusivity of oxygen in precursors. With these assumptions, we can roughly say that the critical height of the film is around the characteristic length scale of oxygen diffusion.

$$H_c \sim \delta \sim 17\mu m$$

Where Hc is the critical height of the PFPE coating.

VI. Movies

Movie S1: The movie is real-time video showing the synthesis of triangular particles in homogeneous PFPE channels. At the channel edges, it is observed that the synthesis channel is expanding during the flow step. The low elastic modulus of PFPE results in the deflection of the rectangular channels under the pressure-driven flows. However, the PFPE channel recovers from the deflected state while the flow stops. The stop time is long enough to allow for the channel relaxation. During the polymerization step, uniform triangular particles are synthesized in the recovered rectangle PFPE channels. The PEG precursor consists of 5% (v/v) Darocur 1173, 40% (v/v) 1X Tris-EDTA buffer, 20% (v/v) PEG 200, and 35% (v/v) PEGDA.

Movie S2: The movie is real-time video showing the synthesis of multifunctional barcoded particles in homogeneous PFPE channels. Different prepolymer mixtures are infused into the three inlets of PFPE channels, generating three coflowing laminar streams. The top and bottom streams consist of PEG precursor with a 200 nm green fluorescent beads, and with 100 nm blue fluorescent beads, respectively. The middle stream is composed of PEG precursor with a fluorescent dye, a methacryloxyethyl thiocarbamoyl rhodamine B. To visualize the middle flow, 5% (v/v) food coloring was added to the stream. An array of multifunctional barcoded particles is produced using SFL in PFPE channels. The throughput of the particle synthesis is 16,000 particles per hour.

References

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