Supplementary Information for:

# Non-spherical particle generation from 4D optofluidic fabrication

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# Supplemental Figures



**Supplemental Fig. S1**. Density dependence on gravity-induced flow shaping. To compare the effects of fluid density differences on core fluid settling, concentration plots for the "E"-channel are shown after pillar P6 for settling times of 0, 20, and 40 s. The sheath fluid density was maintained at  $\rho_{\text{sheath}} = 1107.8 \text{ kg/m}^3$ , while the core fluid density  $\rho_{\text{core}}$  was varied. The percent increase of core-to-sheath density is labeled as  $\Delta \rho$ , and four cases are tested:  $\Delta \rho = 0.00 \%$ , 0.10 %, 0.23 %, and 0.30%. The  $\Delta \rho = 0.23 \%$  case, outlined by the green dashed line, represents the experimentally measured fluid properties, as also shown in Fig. 2B. For no density difference ( $\Delta \rho = 0.00 \%$ ), there is no gravity-induced flow shaping; however, the flow shape changes slightly due to diffusion. The rate of core fluid settling is highly dependent on the density mismatch. Density increases of 0.1 % cause a noticeable increase in core settling rates.



**Supplemental Fig. S2.** Viscosity dependence on gravity-induced flow shaping. To compare the effects of viscosity differences on core fluid settling, concentration plots for the "E"-channel are shown after pillar P6 for settling times of 0, 20, and 40 s. The sheath fluid viscosity was maintained at  $\mu_{\text{sheath}} = 11.2$  mPa·s, while the core fluid viscosity  $\mu_{\text{core}}$  was varied. The percent increase of core-to-sheath viscosity is labeled as  $\Delta\mu$ , and four cases are tested:  $\Delta\mu = 5$  %, 10 %, 15 %, and 20%. The  $\Delta\mu = 5$  % case, outlined by the green dashed line, represents the experimentally measured fluid properties, as also shown in Fig. 2B. Compared to the dependence core fluid settling has on density, as shown in Fig. S1, the viscosity difference only slightly affects gravity-induced flow shaping. When the core viscosity was 20 % larger than the sheath, the core fluid settled slightly slower than the  $\Delta\mu = 5$  % case. This implies that the viscosity difference has a much smaller effect on core settling than the density difference.



**Supplemental Fig. S3.** Diffusion dependence on gravity-induced flow shaping. To compare the effects of the diffusion coefficient *D* on core fluid settling, concentration plots for the "E"-channel are shown after pillar P6 for settling times of 0, 20, and 40 s. Four different values of *D* are tested:  $D = 1 \times 10^{-12} \text{ m}^2/\text{s}$ ,  $D = 4 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D = 1 \times 10^{-10} \text{ m}^2/\text{s}$ , and  $D = 1 \times 10^{-9} \text{ m}^2/\text{s}$ . The  $D = 4 \times 10^{-11} \text{ m}^2/\text{s}$  case, outlined by the green dashed line, represents the experimentally measured fluid properties, as also shown in Fig. 2B. As the diffusion rate increases, more species diffuses out of the core stream, causing the core stream to settle slower. However, when the diffusion coefficient is as large as  $D = 1 \times 10^{-9} \text{ m}^2/\text{s}$ , the flow shape becomes heavily blurred, not ideal for particle fabrication.



**Supplemental Fig. S4: Interactions between core fluid and secondary flow.** Binary concentration slices taken from the simulation results of Fig. 2A are shown for the side pillar channel. (A) The core fluid area shown in gray decreases from P0 to P1. (B) Net streamline displacement plots represent the lateral secondary flows in the y-z plane created after passing a single pair of half-side pillars. (C) Overlays of the streamline displacement plots on the concentration slices shows how the core fluid shape interacts with the secondary flows. Due to the width and size of the core fluid at P0, much of the center of the core fluid experiences inward flow in the center, creating an "I" shape and leading to an area reduction. For pillars after P1, even though the flow experiences the same geometric obstruction (side pillars). The cross sectional area begins to increase. Since the core fluid now has an "I"-shape, this shape allows for significant outward flow motions near the top and bottom due to secondary flow interactions, but relatively weaker inward flows near the center. The size, height, and location of core fluid relative to secondary flow motion will determine the area change after passing a pillar.

### **Supplemental Notes**

#### **Supplemental Note 1**

#### **Measuring fluid properties**

Density measurements

In order to measure the densities of the two precursor fluids, PEG-DA and PEG-DA+DMPA, the two fluids were removed from the refrigerator and allowed to warm up to room temperature. The PEG-DA was pure poly(ethylene glycol) diacrylate  $M_n$  250, while the second fluid was a solution of PEG-DA and 5 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA). The mass of two 50 mL Class A volumetric flasks were measured using a balance with 0.0001 g resolution. 50 mL of each fluid was then transferred to the volumetric flasks using a motorized pipette. The mass of each full volumetric flask was measured. The increase in mass from empty to full flask represented the mass of fluid for a 50 mL volume. The densities were calculated to be as follows:

$$\rho_{PEGDA} = \frac{55.3915 \,g}{50 \,mL} = 1.1078 \,g/mL = 1107.8 \,kg/m^3$$
$$\rho_{PEGDA+DMPA} = \frac{55.5189 \,g}{50 \,mL} = 1.1104 \,g/mL = 1110.4 \,kg/m^3$$

Viscosity measurements

The viscosity of each fluid, PEG-DA and PEG-DA+DMPA, were measured using a TA Instruments AR-G2 Rheometer. 0.5 mL of fluid was transferred to the flat 25 mm sample plate. The plate was heated and maintained at 25°C. As the Peltier Plate rotated and sheared the fluid, ten shear stress measurements were recorded at shear rates between 12 s<sup>-1</sup> to 100 s<sup>-1</sup>. A plot of the shear stress vs shear rate data can be seen below. Linear regression was then performed to calculate the viscosity (shear stress/shear rate). Based on the linear regression analysis, the viscosity of PEG-DA was determined to be 11.2 mPa·s with an adjusted R-squared of 0.999. The viscosity of the PEG-DA + DMPA was determined to be 11.8 mPa·s with an adjusted R-squared of 0.999. This strong linear shear stress vs shear rate relationship indicates Newtonian fluid behavior, as expected.



#### **Supplemental Note 2**

#### Calculating diffusion coefficient

The calculation for the diffusion coefficient of DMPA in PEG-DA was based on the Stokes-Einstein-Sutherland Equation. This equation calculates the rate of diffusion of a sphere through a liquid at low Reynolds numbers. It is assumed that one molecule of DMPA could be treated as a sphere, and the calculation goes as follows:

Stokes-Einstein-Sutherland Equation:

$$D = \frac{k_B T}{6\pi\mu r}$$

where *D* is the diffusion coefficient,  $k_B$  is the Boltzmann constant, *T* is temperature,  $\mu$  is the dynamic viscosity, and *r* is the radius of a DMPA molecule. To calculate the radius of a molecule of DMPA, the molar volume was used to approximate the volume of a single molecule:

$$V_M = \frac{M}{\rho} = \frac{256.3g/mol}{1.210g/cm^3} = 211.82cm^3/mol$$

 $V_M$  represents the molar volume, M is the molar mass, and  $\rho$  is the density of DMPA. The approximate volume of a DMPA molecule was then found as follows:

$$V = \frac{V_M}{N_A} = \frac{211.82 cm^3/mol}{6.022 \times 10^{-23} mol^{-1}} = 3.517 \times 10^{-22} cm^3$$

where V is the volume of a DMPA molecule and  $N_A$  is Avogadro's constant. The radius could then be found using the equation for the volume of a sphere:

$$V = \frac{4}{3}\pi r^3 = 3.517 \times 10^{-22} cm^3$$
  
$$\implies r = \left[\frac{3V}{4\pi}\right]^{1/3} = \left[\frac{3(3.517 \times 10^{-22} cm^3)}{4\pi}\right]^{1/3} = 4.379 \times 10^{-8} cm = 4.379 \times 10^{-10} m$$

The diffusion coefficient was then calculated:

$$D = \frac{k_B T}{6\pi\mu r} = \frac{(1.3806 \times 10^{-23} J/K)(298.15K)}{6\pi (11.2 \times 10^{-3} Pa \cdot s)(4.379 \times 10^{-10} m)} = 4 \times 10^{-11} m^2/s$$

 $D = 4 \times 10^{-11} m^2/s$ 

#### **Supplemental Note 3**

#### **3D** particle fabrication methods comparison

Process	Resolution	Throughput	Cost for equipment
4D optofluidic fabrication	~1 µm [1]	3,600 particles/hour (potentially 10 <sup>5</sup> particles/hour)	~\$5,000 [2]
Stop flow lithography (SFL)	~1 µm [1]	>10 <sup>6</sup> particles/hour [2]	~\$5,000 [2]
PRINT®	~0.4 nm [3]	>10 <sup>12</sup> particles/min [4]	N/A* (cost of creating e-beam lithography based mold [3])
Inkjet 3D Printing	~40 µm [5]	seconds-minutes per particle	~\$20,000 [6]
Stereolithography (SLA)	~50 µm [7]	seconds-minutes per particle	~\$3,500 [8]
Fused deposition modeling (FDM)	~200 µm [5]	seconds-minutes per particle	~\$350 [9]
Two photon polymerization (2PP)	~100 nm [5]	minutes-hours per particle	N/A* (cost of two-photon microscope with Ti- Sapphire laser ~\$1M)

**Table S1:** Comparison between resolution, throughput, and costs associated with the leading 3D particle fabrication methods

The current 4D optofluidic fabrication can fabricate 3,600 particles/hour using the current onmicroscope setup; however, this throughput could be increased to >10<sup>5</sup> particles/hour by using an off-microscope setup with channel parallelization.<sup>10</sup> Additionally, 4D optofluidic fabrication has currently created particles with a minimum feature size near 100  $\mu$ m. In theory, the resolution of 4D optofluidic fabrication should be similar to SLF, but the resolution in the "z" direction can become limited due to diffusion between fluid streams. Finally, if off-microscope particle fabrication is used, the necessary equipment can be expected to cost around \$5,000.<sup>2</sup>

# **Supplemental Movie Captions**

**Supplemental Movie S1: UV Polymerization to reveal cross section.** First, a thin slit of UV light is used to polymerize a thin particle immediately after stopping the flow in the "E"-channel. Tipping this particle over reveals a top-down symmetric particle cross section. Next, 4D optofluidic fabrication is demonstrated by waiting a settling time of t = 40 s to polymerize the thin particle after stopping the flow. A fully asymmetric particle cross section is then revealed.

## References

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