Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Split or slip - passive generation of monodisperse double emulsions with cores of varying viscosity in microfluidic tandem step emulsification system

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Feed W/O emulsion production in flow-focusing device

Single W/O emulsions were generated in a fluorophilic flow-focusing microfluidic device, as it allowed to produce droplets of wide range of sizes in the same device. Examples of produced droplets are shown in Fig. S1

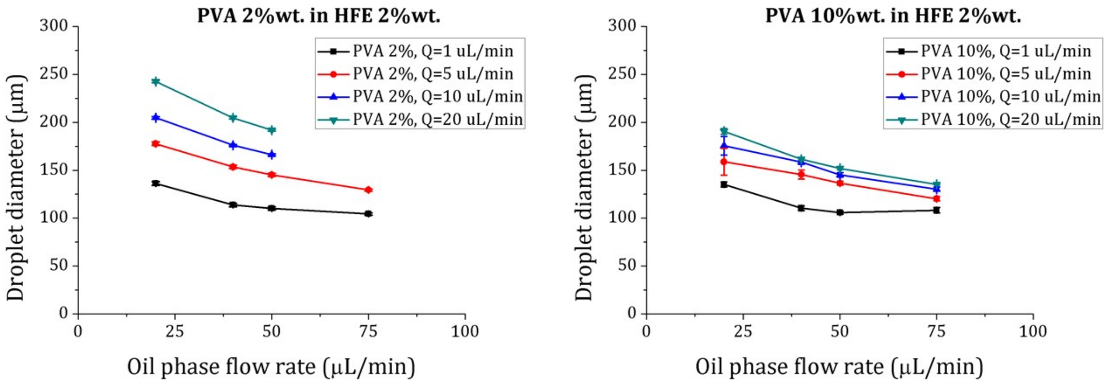

Fig. S1 Water in oil droplets produced in the flow-focusing device. Left: PVA 2%wt. in fluorinated oil (HFE-7500 with 2%wt. surfactant.) Right: PVA 10%wt. in fluorinated oil (HFE-7500 with 2%wt. surfactant).

The flow rates used to produce single emulsion were greater than flow rate used for subsequent double droplet generation. This is because the produced W/O droplets were stored in a tubing connecting two microfluidic devices. Then the flow of all fluids was stopped, and step emulsification module was flushed with fresh portion of aqueous outermost phase of double droplet. Then oil phase was set to Q_{drip}=0.5 ul/min and it pushed W/O emulsion into reservoir filled with outermost phase. The hydrophilic step emulsification device, filled with the outer phase, was placed vertically (inlet above the junction), so the emulsion from the tubing flew downstream to the step emulsification junction. Since the single emulsion was temporarily stored in the tubing for some time with flow turned off, the droplets floated upwards and creamed at the highest point of the tubing. When the flow was turned on again, first the carrier oil liquid was emulsified in the second device (empty oil droplets). The core droplets arrived as a dense emulsion, with small oil spacers between the cores.

Determination of Q_{drip}

We investigated the range of flow rates of the to be dispersed phase to determine the maximum value, Q_{drip}, for which the step emulsification module operated in the dripping regime. We injected aqueous sample into oil-filled fluorophilic device to obtain W/O emulsion, and oil was supplied to water filled hydrophilic device of the same geometry to obtain O/W emulsion. To be dispersed phases were injected at varying flow rates and the size of the droplets was measured and presented in Fig. S2.

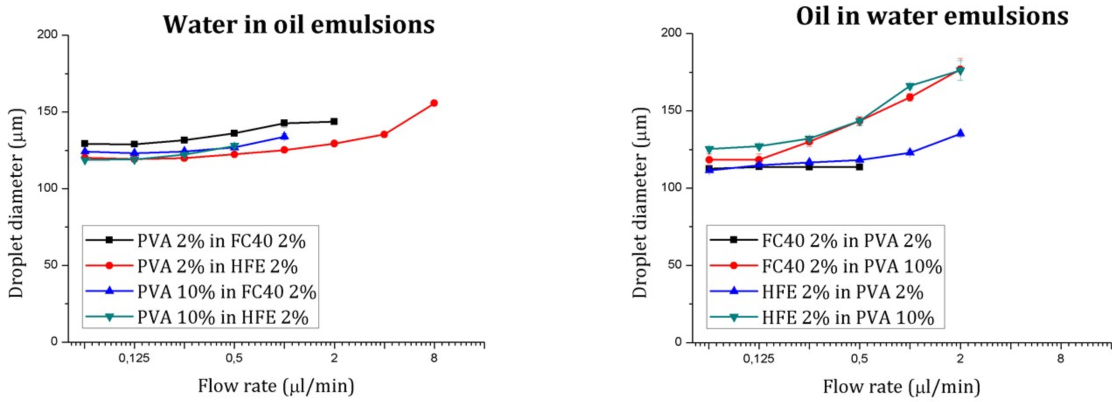

Fig. S2. Formation of single emulsion in step emulsification devices of different surface properties. Left: Size of droplets generated in fluorophilic device (W/O emulsions) as a function of the applied flow rate. Right: Size of droplets generated in hydrophilic device (O/W emulsions) as a function of the applied flow rate.

Nominal droplet diameter d_n

We measured the size of single emulsion droplets formed in our step emulsification system and determined the nominal droplet size, d_n, for Q_{drip}. Step emulsification of single W/O emulsion to W/O/W double emulsion involves both W/O and O/W emulsions, thus we conducted the experiment for both kinds of emulsions and presented them in Table S. 1

Table S. 1 Nominal droplet diameters for investigated systems. λ_{dp} is the viscosity ratio of droplet to outer phase.

Droplet phase	Outer phase	λ_{dp} [-]	d_n [µm]
PVA 2% w/w in water	HFE-7500 2% surfactant	1.5	122.4 ± 1
PVA 2% w/w in water	FC 40 2% surfactant	0.5	136.1 ± 1
PVA 10% w/w in water	HFE-7500 2% surfactant	18.1	127.9 ± 1
PVA 10% w/w in water	FC 40 2% surfactant	5.6	126.8 ± 1
HFE-7500 2% surfactant	PVA 2% w/w in water	0.7	118.2 ± 1
HFE-7500 2% surfactant	PVA 10% w/w in water	0.1	143.4 ± 3
FC 40 2% surfactant	PVA 2% w/w in water	2.1	113.6 ± 1
FC 40 2% surfactant	PVA 10% w/w in water	0.2	143.4 ± 1

Influence of bypasses in passive step emulsification device on formed single emulsions

Bypasses should facilitate droplet formation in step emulsification geometry. To utilize this phenomenon, we designed the geometry with side channels that serve as bypasses. We compared it to a geometry without bypasses (called 'standard'; its side channels enter the reservoir downstream the junction). Results are presented in Fig. S3. Both types of devices produced monodisperse emulsions in the range of rates of flow of 0.05-2 µL/min. Droplets from the bypassed geometry (with side channels) were smaller than from the standard geometry for each investigated flow rate. Smaller droplets and higher stability of the droplet sizes to the variations of the flow rate were the reason we used devices with side channels acting as bypasses in further experiments.

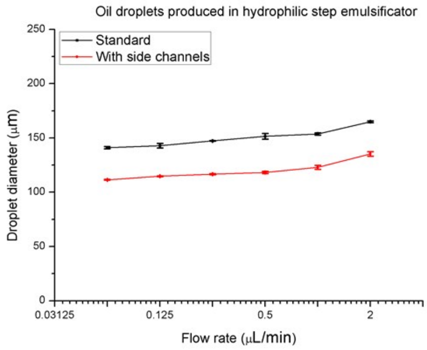

Fig. S3. Sizes of droplet produced in hydrophilic chips of different geometries. Dispersed phase is HFE-7500 with 2%wt. surfactant, continuous phase is PVA 2%wt.