(1) Microfluidic device designs

(a) Long-term stability test

The microfluidic experiment presented in Fig. 2(a) and Fig. 2(b) was performed inside a microfluidic device with a channel height of 25 µm. The chip design is shown in Fig. S1.

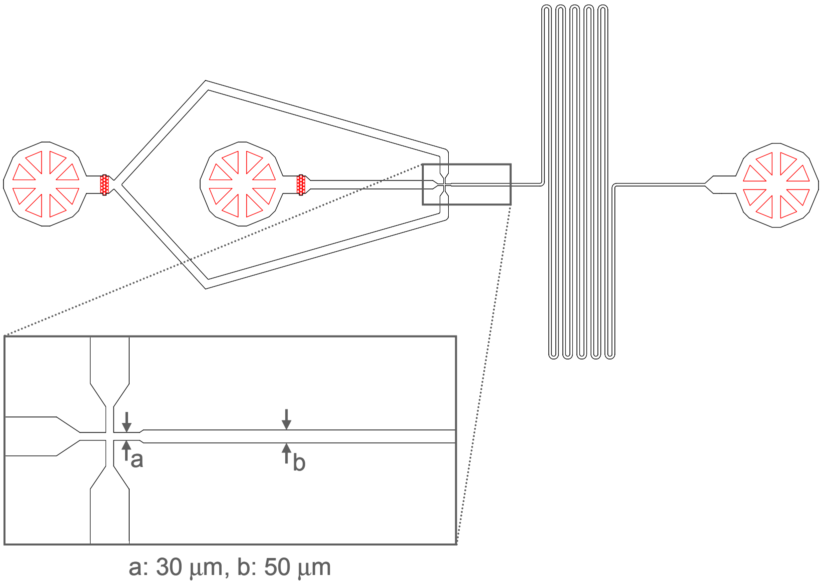

Fig. S1 Design of the device depicted in Fig. 2(a) and Fig. 2(b).

(b) High-throughput o/w droplet formation

A microfluidic chip with a channel height of 25 µm was used for the high-throughput o/w droplet formation depicted in Fig. 3(a) and Fig. 3(b). The device layout is given in Fig. S2.

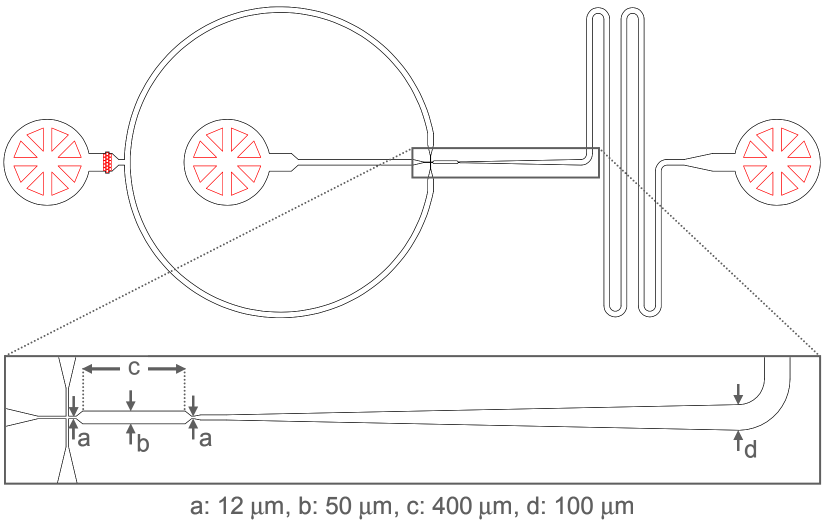

Fig. S2 Design of the device depicted in Fig. 3(a) and Fig. 3(b).

(c) Production of a w/o/w double emulsion

The fluorescence microscopy study presented in Fig. 4(b) to Fig. 4(e) as well as the production of a w/o/w double emulsion depicted in Fig. 5(a) and Fig. 5(b) were performed using a microfluidic device with a channel height of 50 µm. Fig S3 shows the corresponding chip design.

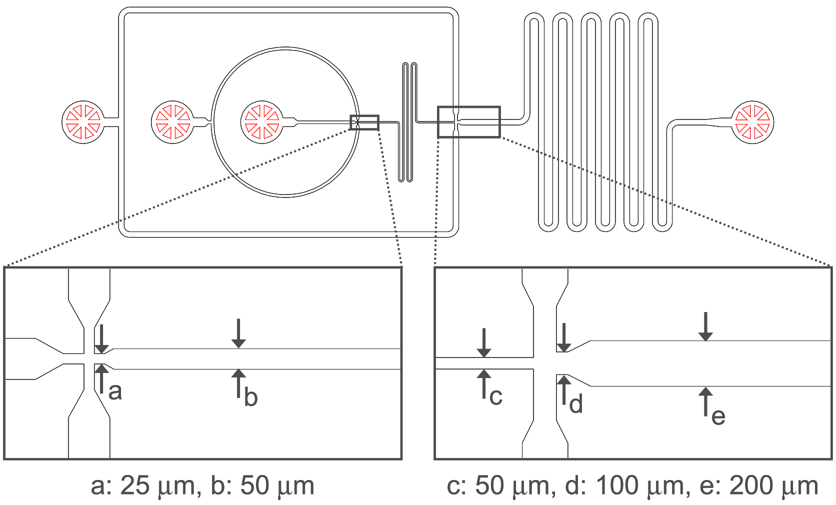

Fig. S3 Design of the device depicted in Fig. 4(b) to Fig. 4(e), Fig. 5(a) and Fig. 5(b).

(2) Movies

(a) M1 – Automated surface modification

This movie illustrates the surface modification of a PDMS based microchannel using our LbL deposition technique. For the sake of clarity solution segments of water being stained with a blue food dye (*SuperCook*) were applied instead of polyelectrolyte solutions. They were stored in a PE tube and pumped through the channel at a constant flow rate of 50 µl/h. The segments enter the microchannel, flush it and are blown out again by the following air plug.

(b) M2 – Long-term stability test

In this movie depicted in Fig. 2(a) the formation of hexadecane in water droplets at an oil flow rate of 50 µl/h and a water flow rate of 150 µl/h is shown. It was taken 80 min after the start of the experiment. The microfluidic chip in use (Fig. S1) had been stored for 165 days between surface modification and droplet production.

(c) M3 – High-throughput o/w droplet formation

The high-speed formation of hexadecane in water droplets at an oil flow rate of 1,000 µl/h and a water flow rate of 4,500 µl/h is captured in this movie, which is depicted in Fig. 3(a). It was taken 35 min after the start of the experiment. Due to the channel design (Fig. S2) the jet breakup is regularized leading to monodisperse droplets. The maximum speed of the camera corresponding to the resolution used was not high enough to follow the droplet formation at a frequency of 13.5 kHz adequately.

(d) M4 – Production of a w/o/w double emulsion

This movie depictured in Fig. 5(b) shows the enclosure of small DIW droplets in bigger FC-40 droplets yielding a monodisperse w/o/w emulsion. Flow rates of 1,500 µl/h for the outer aqueous phase, 200 µl/h for the oil phase and 150 µl/h for the inner water phase were applied. The movie was taken 70 min after starting the experiment. Prior to the microfluidic experiment the device in use (Fig S3) had been turned partially hydrophilic, partially hydrophobic in a two step surface modification process.