Ultra-thin liquid film extraction based on gas-liquid-liquid double emulsion in a microchannel device

(Supporting Information)

Kai Wang, Kang Qin, Guangsheng Luo and Tao Wang

5   *The State Key Lab of Chemical Engineering, Department of Chemical Engineering,*

Tsinghua University, Beijing 100084, China

1. Fabrication of microfluidic device

The microfluidic device was fabricated from polymethyl methacrylate (PMMA) plates with precise mills and sealed to a transparent chip in a high-pressure thermal

10   sealing machine (A274, Techson, China) at 75 ℃, 0.4 MPa. The fluid channels at the cross-junction had the same rectangle cross-sections, whose width (W) and height (H) were 1050 and 970 μm. The monitor chamber was 10 mm at the downstream of the cross-junction, whose width (W_m) and height (H_m) were 2000 and 970 μm. The length of the monitor chamber was 18 mm. The inlets of three-phase microchannels and the

15   monitor chamber outlet were connected to Teflon pipes, whose inner diameter and length were 900 μm and 200 mm. The silica tube with inner and outer diameters of 250 μm and 430 μm was from a chromatography company (Techcomp, China). The tapered glass capillary was made by a micropipette puller (P-97, Sutter, USA). The inner and outer diameters of the capillary tip were 100 and 160 μm and the original

20   inner and outer diameters of the capillary were 750 and 1000 μm. The vertex angle of the taper was 21°.

2. Experimental equipment

The experiment was proceeded in a platform shown by Fig. 1c in the main text. For the observation of microflow, a microscope system was used to record experimental

25   phenomena, including a high speed COMS camera at 130 frames/second (PL-A741U, PixeLINK, Canada), an optical microscope (6 μm/pixel, View Solutions, USA) and a bottom light source. To feed oil and water phases, all the flow rates, ranged from 10 to

800 μL/min, were controlled by syringe pumps (LSP01-2A and LSP02-1B, Longer, China) with gas tight syringes (1 mL or 10 mL). The gas phase used in the experiment was stored in a cylinder (Provided by the Huayuan Gas Co., Ltd., China) and it was fed by the pressure ($0.02 \sim 0.05$ MPa) in a precise regulator (A-2H, Aerotech, USA). The flow rate of gas phase was evaluated from the recorded movies by assuming the velocity of bubbles equal to the average velocity of three-phase $(Q_G+Q_O+Q_W)/WH$. The experimental temperature was 24°C. In running each experiment, the gas phase was firstly fed in and then the oil and water phases were pumped.
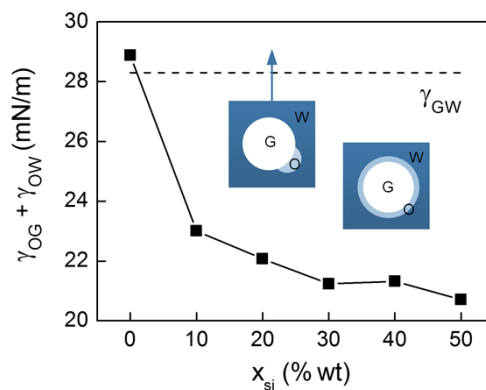

Fig. S1 The effect of silicone oil concentration on the three-phase interfacial tensions. The dash line shows the surface tension of continuous phase.

3. Materials and physical properties

The type of polyvinyl alcohol (PVA) used in the experiment was PVA 1788, which had an average polymerization degree of 1700 (1700 segments of -CH_2-CHOH-) and a hydrolyzing ratio of vinyl acetate (PVA was made by hydrolyzing polyvinyl acetate) of 88%. The average molecule weigh of this PVA 1788 was about 83000 and it was provided by Aladdin chemistry Co. Ltd. The 1-phenylazo-2-naphthalenol (Sudan IV) was brought from Aladdin chemistry Co. Ltd. too. The sodium dodecyl sulfate (SDS), n-octane and silicon oil (50 mPa·s) were provided by Sinopharm Chemical Reagent Co., Ltd. Physical properties of all the working systems used in this study are listed in Table S1. In this table, the density and viscosity of air were collected from a handbook pressed by the Chemical Industry Press, Beijing.[1] The liquid densities were measured with densitometers and viscosities were measured with Ubbelohde

viscometers. The interfacial tensions were measured with a tensiometer (OCAH200, DataPhysics Instruments GmbH, Germany). Fig. S1 shows the effect of silicone oil concentration on the three-phase interfacial tensions. The gas-liquid-liquid double emulsion fits the rule of $\gamma_{GW} > \gamma_{OW} + \gamma_{GO}$ with the help of silicone oil. The solubility data of Sudan IV in octane and silicone oil were measured by the UV-visible spectrophotometer and the results are 0.216g/100g octane and 0.0012g/100g silicone oil at 24 °C.

Table. S1 Physical properties of the working systems (24 ℃, 1 atm)

Phases	Fluids	Viscosities μ (mPa·s)	Densities ρ (g/mL)	Surface tensions γ_{GW} or γ_{GO} (mN/m)	Interfacial tensions γ_{WO} (mN/m)
Water (Outer)	0.5 wt% SDS, 1 wt% PVA solution	2.79	1.036	28.3	-
Oil (middle)	n-octane	0.58	0.703	23.2	5.65
	10 wt% silicone oil octane solution	0.82	0.726	21.8	1.22
	20 wt% silicone oil octane solution	1.17	0.748	21.6	0.43
	30 wt% silicone oil octane solution	1.66	0.757	20.9	0.36
	40 wt% silicone oil octane solution	2.27	0.767	20.9	0.38
	50 wt% silicone oil octane solution	3.36	0.790	20.3	0.36
Gas (inner)	air	0.017	0.0012	-	-

4. Bubble coalescence phenomenon at the capillary tip

The phenomenon of bubble coalescence at the capillary tip is interesting and its details are given in Fig. S2. It is clear the gas phase break-up in the trapped capillary in Figs. S2b and S2f. Usually, these earlier break-up will produce small bubbles in the downstream channel in a gas-liquid flow system. However, according to Figs. S2c and Figs. S2g, the generated bubble does not leave the capillary tip with the trap of oil film, therefore the followed gas phase collides the earlier generated bubble and the coalescence makes bubble grow until it is big enough to obtain enough force from the continuous phase. The bubble coalescence is the result that none surfactant was used

in the oil phase, which is different from previous studies in the material perpetration process.[2] Since the bubble size is not determined by the flows in the trapped capillary, 70 the finial bubble diameters do not change very much.
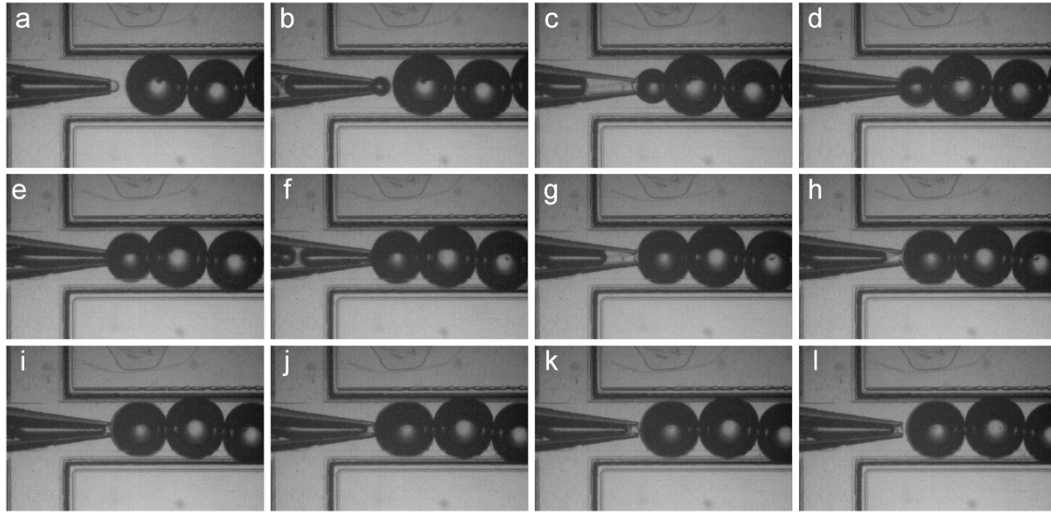

Fig. S2 The picture sequence in a double emulsion generation process. The details are x_{si} = 10wt%, p_G = 0.029 MPa, Q_G = 1990 μL/min, Q_O = 25 μL/min, Q_W = 400 μL/min.

5. Operating parameters of the movies

75 Movie 1: x_{si} = 20wt%, p_G = 0.038 MPa, Q_G = 2540 μL/min, Q_O = 30 μL/min, Q_W = 600 μL/min.

Movie 2: x_{si} = 10wt%, p_G = 0.029 MPa, Q_G = 1990 μL/min, Q_O = 25 μL/min, Q_W = 400 μL/min;

and C_{si} = 10wt%, p_G = 0 MPa, Q_G = 0 μL/min, Q_O = 25 μL/min, Q_W = 400 μL/min.

6. References

(1) G. Q. Liu, L. X. Ma and J. Liu, *Chemistry and chemical property data manual*, 80   Chemical Industry Press, Beijing, 2002.

(2) R. Chen, P. F. Dong, J. H. Xu, Y. D. Wang and G. S. Luo, *Lab Chip*, 2012, 12, 3858-3860.