A Novel Surgery-like Strategy for Droplet Coalescence in Microchannels

Supplementary material

Nan-Nan Deng, a Shao-Xing Sun, a Wei Wang, a Xiao-Jie Ju, a Rui Xie a and Liang-Yin Chu* a,b

a School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, China.
E-mail: chuly@scu.edu.cn (L.-Y. Chu); Fax & Tel: +86 28 8546 0682
b State Key Laboratory of Polymer Materials Engineering, and Collaborative Innovation Center for Biomaterials Science and Technology, Sichuan University, Chengdu, Sichuan, 610065, China

Part I. Supplementary Experimental Details.

Part II. Supplementary Table S1 and Figures S1-S8.

Part III. Supplementary Movies S1-S5.
Part I. Supplementary Experimental Details

Materials
To prepare W/O emulsion droplets, aqueous solution containing 0.5~1 % (w/v) sodium dodecyl sulfate (SDS) or 0.5~2% (w/v) Pluronic F-127 (F127, Sigma-Aldrich) and silicone oil (SiO) (10 cSt, Jinan Yingchuang Chemicals) containing 0~5 % (w/v) Dow Corning 749 (DC749, Dow Corning Corporation), are employed as the disperse and continuous phases, respectively. To prepare O/W/O emulsion droplets, soybean oil (SO) containing 1 % (w/v) polyglycerol polyricinoleate (PGPR90), aqueous solution containing 1 % (w/v) SDS, and SiO containing 1 % (w/v) DC749 are respectively used as the inner, middle and outer phases. In addition, SiO containing 0.5 % (w/v) calcium carbonate nanoparticles (nano-CaCO₃, average particle diameter of 300 nm), SO containing 0.5~1 % (w/v) PGPR90, and benzyl benzoate (BB) containing 1 % (w/v) PGPR90 are also utilized respectively as oil phases in the experiments for further demonstrations. To make chitosan microspheres and microcapsules via the coalescence-induced microreaction, deionized water containing 2.0 % (w/v) chitosan ($M_w=5000$, degree of deacetylation 85 %) and 0.5 % (w/v) F-127, and another aqueous solution containing 0.1 % (w/v) terephthalaldehyde and 0.5 % (w/v) SDS, are utilized as two aqueous phases. All the SDS, F-127, PGPR90, nano-CaCO₃ and DC749 are used as surfactants or stabilizers to assist the formation of emulsions and prevent undesired coalescence.

Set up and characterization
All the microchannels are fabricated by bonding patterned coverslips (thickness of 130~170 µm) to a microscope glass slide in designed geometries with a UV-curable adhesive, and then a polyethylene pipe and several syringe needles are connected as the outlet and inlets. To
generate water-in-oil (W/O) emulsions and oil-in-water-in-oil (O/W/O) double emulsions, the surface wettability properties of microchannels are modified spatially by self-assembled monolayer (SAM) chemistry and flow confinement method.[S1]

Syringes and syringe pumps (LSP01-1A, Baoding Longer Precision Pumps) are used for driving fluids flow into the microchannels. The formation and fusion processes of droplets are observed by an inverted optical microscope (IX71, Olympus) equipped with a high speed camera (Miro3, Phantom, Vision Research). The prepared chitosan microspheres and microcapsules are observed by a confocal laser scanning microscope (CLSM, SP5-II, Leica) with excitation at approximate 488 nm. All the experiments are carried out at room temperature.

Supplementary Reference

### Part II. Supplementary Table S1 and Figures S1-S8

**Table S1.** Effects of micro-lancet features on the coalescence of W/O emulsion droplets in different continuous oil phases.

<table>
<thead>
<tr>
<th>Oil phase</th>
<th>Surfactant in oil phase</th>
<th>Surfactant concentration in oil (wt.%)</th>
<th>Micro-lancet</th>
<th>Coalescence (YES or NO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>DC749</td>
<td>0.0~1.0</td>
<td>√</td>
<td>NO</td>
</tr>
<tr>
<td>SiO</td>
<td>DC749</td>
<td>0.0~1.0</td>
<td>√</td>
<td>NO</td>
</tr>
<tr>
<td>SiO</td>
<td>DC749</td>
<td>0.0~5.0</td>
<td>√</td>
<td>YES</td>
</tr>
<tr>
<td>SiO</td>
<td>Nano-CaCO₃</td>
<td>0.5</td>
<td>√</td>
<td>NO</td>
</tr>
<tr>
<td>SiO</td>
<td>Nano-CaCO₃</td>
<td>0.5</td>
<td>√</td>
<td>YES</td>
</tr>
<tr>
<td>SO</td>
<td>PGPR90</td>
<td>0.5</td>
<td>√</td>
<td>NO</td>
</tr>
<tr>
<td>SO</td>
<td>PGPR90</td>
<td>0.5~1.0</td>
<td>√</td>
<td>YES</td>
</tr>
<tr>
<td>BB</td>
<td>PGPR90</td>
<td>1.0</td>
<td>√</td>
<td>NO</td>
</tr>
<tr>
<td>BB</td>
<td>PGPR90</td>
<td>1.0</td>
<td>√</td>
<td>YES</td>
</tr>
</tbody>
</table>

*Note:* The water phases in the W/O emulsions are aqueous solutions containing 0.5~2.0 wt % F127 or 0.5~1.0 wt % SDS.
Figures

**Fig. S1.** Coalescence of W/O emulsion droplets induced by a plastic micro-lancet with hydrophilic surface and knife-like tip.
Fig. S2. Effect of the tip shape of micro-lancets on the coalescence of W/O emulsion droplets. (a) Schematic illustration of micro-lancet-induced coalescence of different W/O emulsion droplets; (b,c) High-speed snapshots of the formation of different W/O emulsions (phase B is dyed with methylene blue trihydrate); (d,e) High-speed snapshots of the droplet coalescence processes induced by copper micro-lancets with hydrophilic surfaces and sharp tip (d) or flat tip (e). The flow rates for (b,c,d) are $Q_A = 400$ µL h$^{-1}$, $Q_B = 200$ µL h$^{-1}$, $Q_{C(upper)} = 200$ µL h$^{-1}$, $Q_{C(lower)} = 150$ µL h$^{-1}$; and those for (e) are $Q_A = 180$ µL h$^{-1}$, $Q_B = 150$ µL h$^{-1}$, $Q_{C(upper)} = 300$ µL h$^{-1}$, $Q_{C(lower)} = 300$ µL h$^{-1}$. 

Electronic Supplementary Material (ESI) for Lab on a Chip
This journal is © The Royal Society of Chemistry 2013
Fig. S3. Effects of the length of micro-lancets on the droplet coalescence. (a) Hydrophilic copper micro-lancet with relatively short length, (b) hydrophilic copper micro-lancet with relatively long length.
**Fig. S4.** High-speed snapshots of the coalescence process of two W/O emulsion droplets.

The coalescence is firstly triggered by the micro-lancet tip, and then spreads along the contact area.
Fig. S5. (a) The schematic illustration of micro-lancet-induced coalescence between W/O emulsion droplets and O/W/O emulsion droplets. (b,c) High-speed snapshots of the preparation of O/W/O emulsions (b) and W/O emulsions (c), respectively. (d,e) High-speed snapshots of the coalescence processes of W/O emulsion droplets and O/W/O emulsion droplets with either relatively thick shells (d) or ultra-thin shells (e). The flow rates for (b,c,d) are $Q_{D1} = 150$ μL h$^{-1}$, $Q_{A} = 200$ μL h$^{-1}$, $Q_{C(upper)} = 200$ μL h$^{-1}$, $Q_{B} = 150$ μL h$^{-1}$, $Q_{C(lower)} = 200$ μL h$^{-1}$; those for (e) are $Q_{D1} = 80$ μL h$^{-1}$, $Q_{A} = 40$ μL h$^{-1}$, $Q_{C(upper)} = 50$ μL h$^{-1}$, $Q_{B} = 100$ μL h$^{-1}$, $Q_{C(lower)} = 120$ μL h$^{-1}$.
Fig. S6. (a) The schematic illustration of micro-lancet-induced coalescence between W/O emulsions and O/W/O emulsions with two different interior droplets. (b,c) High-speed snapshots of the formation of dual-core O/W/O emulsions (g) and W/O emulsions (h), respectively. (d,e) High-speed snapshots of the coalescence processes of W/O emulsion droplets and dual-core O/W/O emulsion droplets with either relatively thick shells (d) or ultra-thin shells (e). The flow rates for (b,c,d) are \( Q_A = 100 \, \mu \text{L h}^{-1} \), \( Q_{D1} = 80 \, \mu \text{L h}^{-1} \), \( Q_{D2} = 80 \, \mu \text{L h}^{-1} \), \( Q_{C(upper)} = 50 \, \mu \text{L h}^{-1} \), \( Q_B = 120 \, \mu \text{L h}^{-1} \), \( Q_{C(lower)} = 100 \, \mu \text{L h}^{-1} \); and for (e) are \( Q_A = 50 \, \mu \text{L h}^{-1} \), \( Q_{D1} = 80 \, \mu \text{L h}^{-1} \), \( Q_{D2} = 80 \, \mu \text{L h}^{-1} \), \( Q_{C(upper)} = 80 \, \mu \text{L h}^{-1} \), \( Q_B = 120 \, \mu \text{L h}^{-1} \), \( Q_{C(lower)} = 100 \, \mu \text{L h}^{-1} \).
Fig. S7. Micro-lancet-induced coalescence between more complex emulsions. (a) High-speed snapshot of micro-lancet-induced coalescence between W/O emulsion droplets and O/W/O emulsion droplets with three interior droplets, (b) High-speed snapshot of micro-lancet-induced coalescence between O/W/O emulsions and O/W/O emulsions with two inner droplets.
Fig. S8. Synthesis of chitosan microspheres and microcapsules in microchannels triggered by micro-lancet-induced coalescence of emulsion droplets. (a) CLSM images of chitosan microspheres fabricated by micro-lancet-induced coalescence between two W/O single emulsion droplets, (b) CLSM images of a chitosan microcapsule fabricated by micro-lancet-induced coalescence between W/O single emulsion droplets and O/W/O double emulsion droplets, in which the oil core inside the chitosan microcapsule is dyed in red color.
Part III. Supplementary Movies S1-S5

**Supplementary Movie S1.** Micro-lancet-induced coalescence of W/O emulsion droplets and the control experiment.

**Supplementary Movie S2.** Coalescences of W/O emulsion droplets induced by micro-lancets with different tips.

**Supplementary Movie S3.** Micro-lancet-induced coalescences between W/O single emulsion droplets and O/W/O double emulsion droplets.

**Supplementary Movie S4.** Micro-lancet-induced coalescence of O/W/O double emulsion droplets for controllably generating emulsions with more complex interior structures.

**Supplementary Movie S5.** Micro-lancet-induced coalescence of two W/O emulsion droplets and one O/W/O double emulsion droplet.