Supplementary Material (ESI) for Lab on a Chip
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Wetting-Induced Formation of Controllable Monodisperse Multiple Emulsions in Microfluidics

Supplementary material

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Part I. Supplementary Note

Part II. Supplementary Figures S1-S7.

Part III. Supplementary Movies S1-S3.

Part I. Supplementary Note

Calculation of the spreading coefficients.

In our experiments, the fluids used for wetting-induced formation of double emulsions (Fig. 1) are listed as follows. Fluid A1 is SO containing 1 wt.% PGPR 90, Fluid A2 is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, Fluid B is water containing1 wt.% SDS, and Fluid C is SiO containing1 wt.% DC749.

Based on the Eqn (4), conclusions can be drawn as folows: When $\gamma_{BC} > \gamma_{AC} + \gamma_{AB}$, *i.e.*, S_A is always positive, drop A engulfs drop B, forming B/A/C double emulsions (Figure 1a3). This process has no relationship with the radius ratio of R_A/R_B. When $\gamma_{AC} + \gamma_{AB} > \gamma_{BC} > \gamma_{AB}$, the engulfing process of drop A and drop B depends on the radius ratio of R_A/R_B. The larger the radius ratio of R_A/R_B, the smaller value of α. As long as S_A is positive, drop A will entirely engulf drop B. When $\gamma_{BC} < \gamma_{AB}$, drop A cannot engulf drop B.

Case 1 (Drop A1 engulfing drop B, as shown in Fig. 1a3):

For drop B and drop A1 dispersed in continuous phase C:

$\gamma_{A1B} = 0.18$ mN m^{-1}, $\gamma_{BC} = 3.07$ mN m^{-1}, $\gamma_{A1C} = 1.37$ mN m^{-1}.

So, $\gamma_{A1B} + \gamma_{A1C} = 1.55 < 3.07$, *i.e.*, $\gamma_{BC} > \gamma_{A1B} + \gamma_{A1C}$.

That is to say, the value of S_{A1} is always larger than 0. Thus, drop A1 can always completely engulf drop B in spite of drop sizes (Fig. 1a3, d, f, g).

Case 2 (Drop B engulfing drop A2, as shown in Fig. 1a4):

For drop B and drop A2 dispersed in continuous phase C:

$\gamma_{A2B} = 0.58$ mN m^{-1}, $\gamma_{BC} = 3.07$ mN m^{-1}, $\gamma_{A2C} = 3.16$ mN m^{-1}.

For $S_B > 0$, we get $R_B/R_{A2} > 0.49$ with the similar derivations in Eqn (1) to (4). That is, when the value of R_B/R_{A2} is larger than 0.49, drop B can completely engulf drop A2, forming A2/B/C double emulsions (Fig. 1a4, e, h, i).

Part II. Supplementary Figures S1-S7:

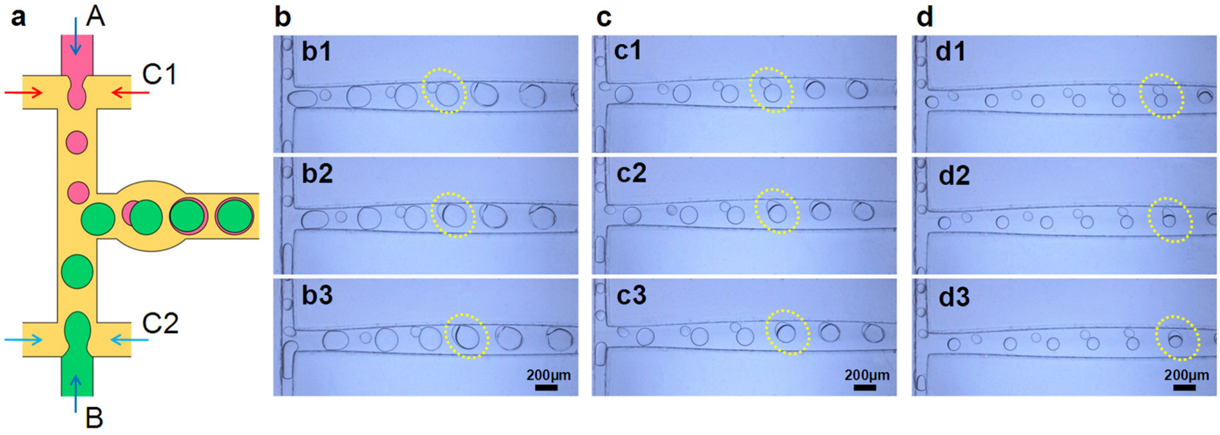

Fig. S1. Wetting-induced formation of double emulsions with controllable core/shell ratios. (a) The schematic of complete spreading of drop A over drop B to form B/A/C emulsions in designed microchannels, in which fluid A is SO containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. (b-d) High-speed optical micrographs of the wetting-induced formation of double emulsions with different core/shell ratios. The flow rates are: (b) Q_A= 20 μL h^{-1}, Q_{C1}= 40 μL h^{-1}, Q_B= 200 μL h^{-1} and Q_{C2}= 300 μL h^{-1}; (c) Q_A= 80 μL h^{-1}, Q_{C1}= 70 μL h^{-1}, Q_B= 150 μL h^{-1} and Q_{C2}=300 μL h^{-1}; (d) Q_A= 40 μL h^{-1}, Q_{C1}= 40 μL h^{-1} , Q_B= 150 μL h^{-1} and Q_{C2}= 500 μL h^{-1}. Scale bars, 200 μm.

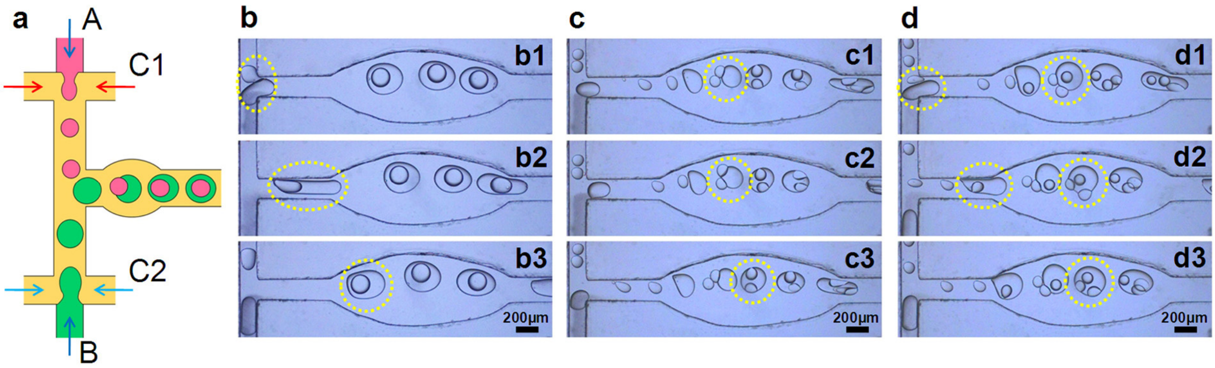

Fig. S2. Wetting-induced formation of double emulsions with controllable number of inner drops. (a) The schematic of entire engulfing of drop A by drop B to form A/B/C emulsions in designed microchannels, in which fluid A is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. (b-d) High-speed snapshots of the wetting-induced formation of double emulsions with one (b), two (c) or three (d) inner drops. The flow rates are: (b) Q_A= 50 μL h^{-1}, Q_{C1}= 100 μL h^{-1}, Q_B= 100 μL h^{-1} and Q_{C2}= 200 μL h^{-1}; (c) Q_A= 80 μL h^{-1}, Q_{C1}= 150 μL h^{-1}, Q_B= 100 μL h^{-1} and Q_{C2}= 400 μL h^{-1}; (d) Q_A= 90 μL h^{-1}, Q_{C1}= 150 μL h^{-1}, Q_B= 200 μL h^{-1} and Q_{C2}= 200 μL h^{-1}. Scale bars, 200 μm.

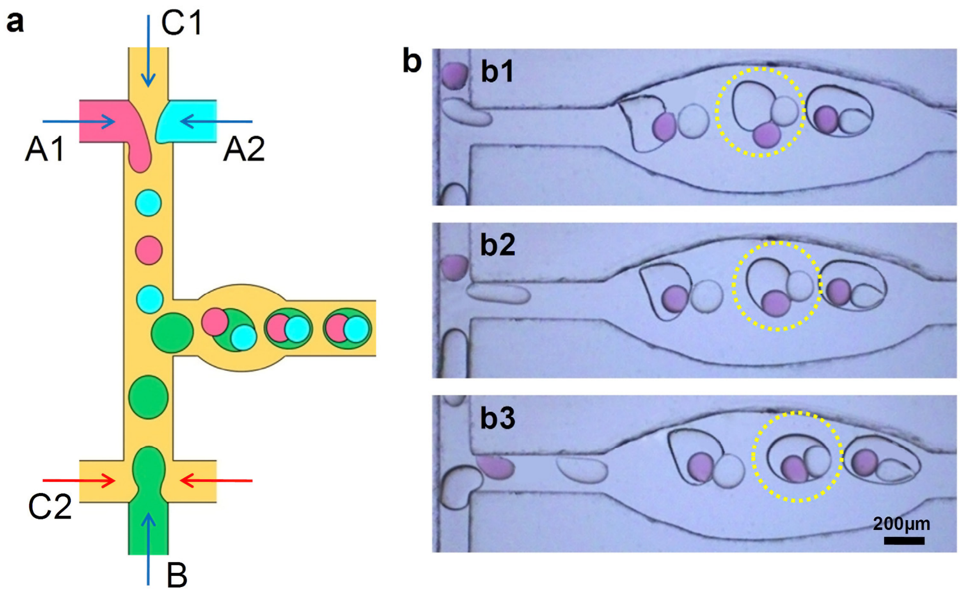

Fig. S3. Wetting-induced formation of double emulsions with different inner drops. The schematic (a) and high-speed optical micrographs (b) of complete engulfing of two different oil drops by one water drop to form double emulsions with two different inner cores. Fluid A1 is SO/Octanol (3:1, v/v) containing 1 % PGPR 90 (w/v) and 1 mg mL^{-1} LR 300, fluid A2 is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. The flow rates are: Q_{A1}= 20 μL h^{-1}, Q_{A2}= 20 μL h^{-1}, Q_{C1}= 200 μL h^{-1}, Q_{B}= 150 μL h^{-1} and Q_{C2}= 400 μL h^{-1}. Scale bar, 200 μm.

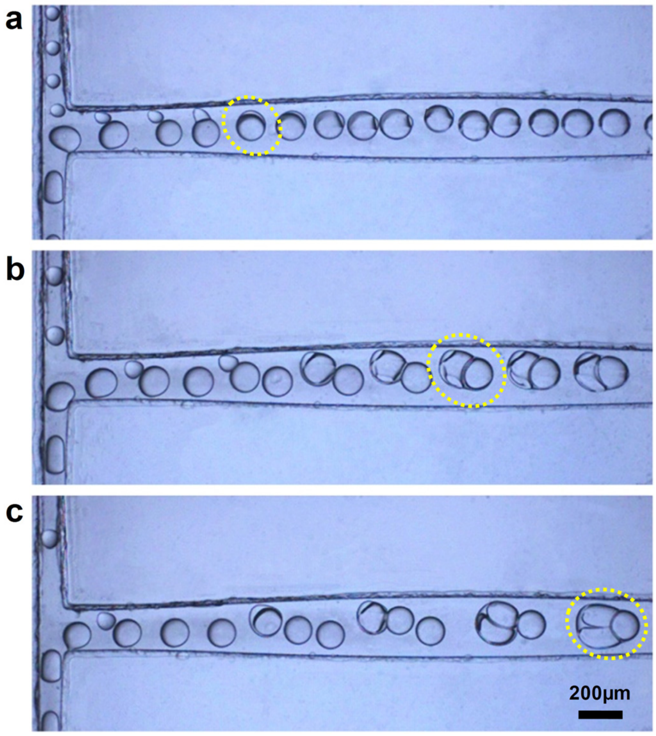

Fig. S4. Wetting-induced formation of double emulsions with ultra-thin shells and controllable number of inner drops. High-speed optical micrographs of the spreading of one small oil drop over one (a), two (b) or three (c) bigger water drops to form double emulsions with ultra-thin shells and different number of inner cores. The schematic of the microfluidic device is the same as Figure S1a. The flow rates are: (a) Q_A= 50 μL h^{-1}, Q_{C1}= 100 μL h^{-1}, Q_B= 200 μL h^{-1} and Q_{C2}= 200 μL h^{-1}; (b) Q_A= 50 μL h^{-1}, Q_{C1}= 100 μL h^{-1}, Q_B= 300 μL h^{-1} and Q_{C2}= 200 μL h^{-1}; (c) Q_A= 50 μL h^{-1}, Q_{C1}= 200 μL h^{-1}, Q_B= 300 μL h^{-1} and Q_{C2}= 200 μL h^{-1}. Scale bar, 200 μm.

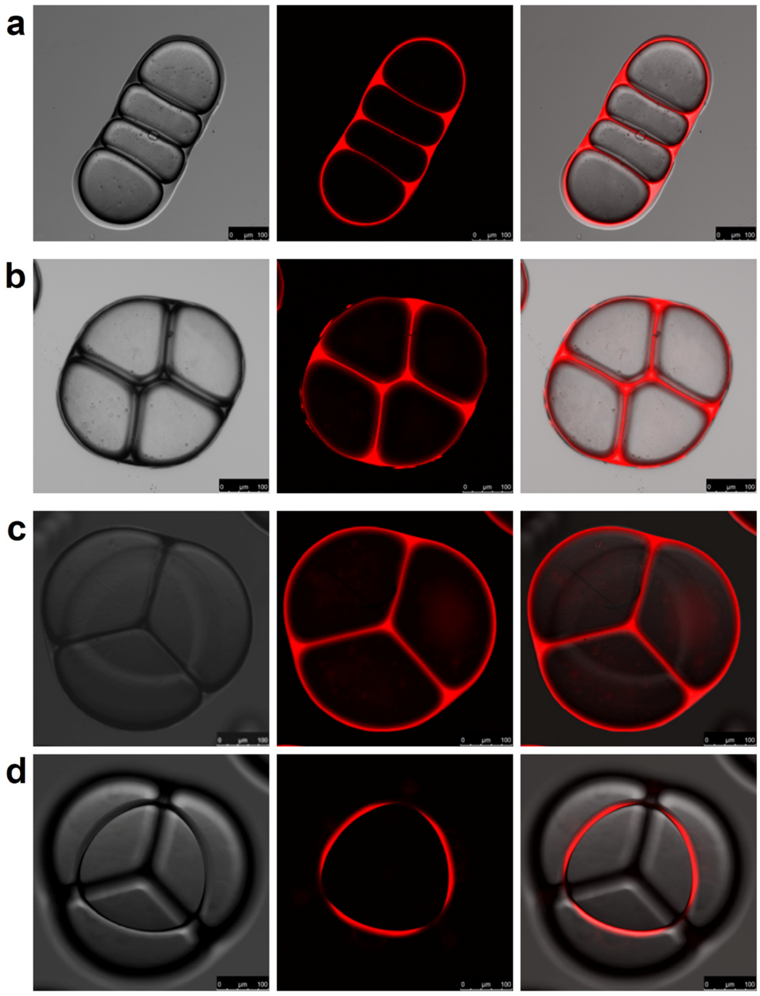

Fig. S5. Diverse configurations of ultra-thin shelled W/O/O double emulsions with four inner drops. CLSM images of ultra-thin shelled W/O/O double emulsions with four inner drops showing three different configurations as linear (a), planar (b) and tetrahedral (c, d) arrangements. Scale bars, 100 μm.

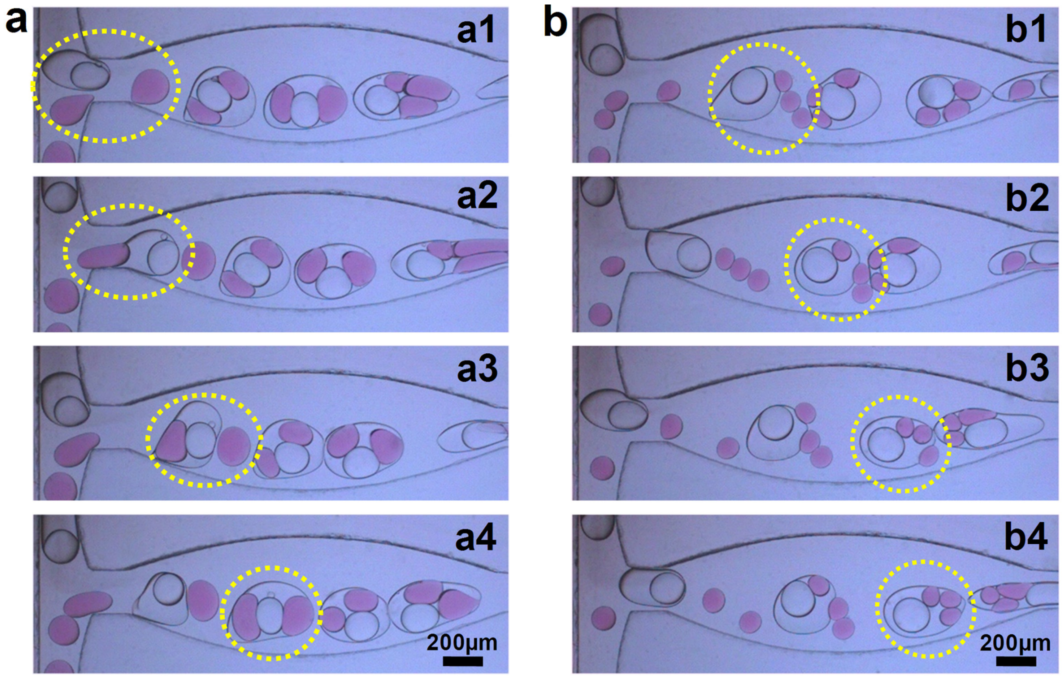

Fig. S6. One O/W/O double emulsion drop completely engulfs two or three O/O single emulsion drops. High-speed snapshots of the complete spreading of one O/W/O double emulsion drop over two (a) or three (b) precursor O/O single emulsion drops to form (O1+O2+O2)/W/O (b) and (O1+O2+O2+O2)/W/O (c) multiple emulsions in detail. The flow rates for case a are: Q_{A2}= 200 μL h^{-1}, $Q_{C(lower)}$= 200 μL h^{-1}, Q_D= 150 μL h^{-1}, Q_B= 150 μL h^{-1}, and $Q_{C(upper)}$ = 300 μL h^{-1}; and those for case b are: Q_{A2}= 200 μL h^{-1}, $Q_{C(lower)}$= 300 μL h^{-1}, Q_D= 150 μL h^{-1}, Q_B= 150 μL h^{-1}, and $Q_{C(upper)}$= 300 μL h^{-1}; and those for Fig. 4e are: Q_{A2}= 50 μL h^{-1}, $Q_{C(lower)}$= 100 μL h^{-1}, Q_D= 150 μL h^{-1}, Q_B= 150 μL h^{-1} and $Q_{C(upper)}$= 300 μL h^{-1}. Scale bars, 200 μm.

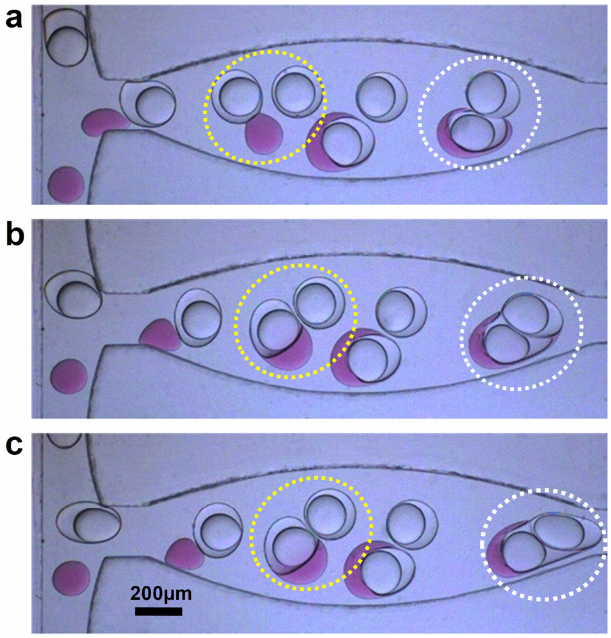

Fig. S7. One O/O single emulsion drop completely engulfs two O/W/O double emulsion drops. High-speed snapshots of the complete spreading of one O/O single emulsion drop over two O/W/O double emulsion drops to form O/W/O/O triple emulsions with two double emulsion drops as cores in detail. The flow rates are: Q_{A1}= 150 μL h^{-1}, $Q_{C(lower)}$= 200 μL h^{-1}, Q_{D}= 250 μL h^{-1}, Q_{B}= 100 μL h^{-1} and $Q_{C(upper)}$= 500 μL h^{-1}; and those for Fig. 5c are: Q_{A1}= 200 μL h^{-1}, $Q_{C(lower)}$= 200 μL h^{-1}, Q_{D} = 150 μL h^{-1}, Q_{B}= 150 μL h^{-1} and $Q_{C(upper)}$= 300 μL h^{-1}. Scale bar, 200 μm.

Part III. Supplementary Movies S1-S3:

Supplementary Movie S1. Wetting-induced formation of double emulsions with controllable core/shell ratios.

Supplementary Movie S2. Wetting-induced formation of double emulsions with controllable number of inner drops.

Supplementary Movie S3. Wetting-induced formation of double emulsions containing different inner drops and triple emulsions.