Lab on a Chip

Wetting-induced formation of controllable monodisperse multiple emulsions in microfluidics†

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Multiple emulsions, which are widely applied in a myriad of fields because of their unique ability to encapsulate and protect active ingredients, are typically produced by sequential drop-formations and drop-encapsulations using shear-induced emulsification. Here we report a qualitatively novel method of creating highly controlled multiple emulsions from lower-order emulsions. By carefully controlling the interfacial energies, we adjust the spreading coefficients between different phases to cause drops of one fluid to completely engulf other drops of immiscible fluids; as a result multiple emulsions are directly formed by simply putting preformed lower-order emulsion drops together. Our approach has highly controllable flexibility. We demonstrate this in preparation of both double and triple emulsions with a controlled number of inner drops and precisely adjusted shell thicknesses including ultra-thin shells. Moreover, this controllable drop-engulfing-drop approach has a high potential in further investigations and applications of microfluidics. Importantly, this innovative approach opens a window to exploit new phenomena occurring in fluids at the microscale level, which is of great significance for developing novel microfluidics.

Introduction

Multiple emulsions are nested systems of drops with one fluid in a second fluid that is dispersed in a third immiscible fluid. Owing to their unique ability to encapsulate and protect active ingredients, multiple emulsions are widely applied in a myriad of fields, such as drug delivery systems,[1,2] food additives or nutriceuticals,[3,4] cosmetics,[5] chemical separations,[6] controlled microreactors,[7] or droplet networks.[8] Multiple emulsions are typically produced by sequential shear-induced emulsifications. For example, to generate double emulsions, the inner drops are produced at the first step, and then encapsulated by the outer drops at the second emulsification step. This leads to highly polydisperse structures because of the randomness intrinsic to each step. More uniform structures can be produced by relatively well-controlled shear with Couette devices[9] or porous membranes[10] for both emulsification steps,

but precise control over the number and size of the interior droplets is still challenging. Microfluidic techniques offer an alternative method for creating multiple emulsions with perfect monodispersity and diverse structures where the number, size and nature of the internal drops are precisely and independently controlled.[11–14] This control over multiple emulsions makes it possible to create various important structures, including polymersomes,[15] colloidosomes,[16] Janus particles,[17] non-spherical particles,[18] microcapsules[19] and microgels,[14] which have great potential for diverse applications. However, current microfluidic techniques for preparing multiple emulsions are mostly achieved in tailored devices that are usually either complicated to construct or difficult to modify, such as multistage assembled micro-capillary devices[13,20] or lithographically-prepared devices.[12,21] These methods also crucially depend on the precise control of the flows at each stage to obtain a stable emulsification process either sequentially[12,14] or simultaneously.[11,22] Furthermore, current microfluidic methods still have certain restrictions, for example, in preparing ultra-thin-shelled double emulsions of different inner drops that are less resistant to mass transfer of multi-component ingredients. Consequently, development of simpler methods for creating controllable monodisperse multiple emulsions is of great value and significance.

In this paper, we present a qualitatively new strategy for making highly controllable monodisperse multiple emulsions from lower-order emulsion drops. By carefully controlling the

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† Electronic supplementary information (ESI) available: Movies S1–S3 and Fig. S1–S7 show the wetting-induced formation of double emulsions and triple emulsions with controllable core/shell ratios and the number of inner drops. The Supplementary Note shows the calculation of the spreading coefficients. See DOI: 10.1039/c3lc50638j

interfacial energies, we adjust the spreading coefficients between different phases to cause drops to completely engulf other drops, thereby directly forming multiple emulsions by putting preformed drops together. This wetting-induced drop-engulfing-drop approach shows exceptional flexibility in making controllable monodisperse multiple emulsions. We produce both double and triple emulsions with a controlled number of inner drops including both single and double emulsion drops, and with precisely adjusted shell thicknesses including ultra-thin shells. In addition, our approach provides a novel and valuable concept to precisely manipulate small volumes of fluids at the microscale level.

Theory and criterion

When drops of two immiscible liquids suspended in a third immiscible liquid are brought into contact, three equilibrium configurations can be created as follows:[23,24] 1) non-engulfing (the two drops remain separated by the matrix phase), 2) partial engulfing (a doublet of drops), and 3) complete engulfing (one drop completely engulfs the other one). The three different morphologies have diverse potential applications.

The basis for the method for formation of multiple emulsions used here is the exploitation of interfacial energies. If the total interfacial energies are reduced, one drop can completely engulf a second. This provides a means of forming a multiple emulsion directly from two drops. The criterion for multiple emulsion formation can be parameterized by the spreading coefficient of the engulfing drop A over the engulfed drop B, as illustrated in Fig. 1a. We assume that the engulfing process is determined by the three interfacial tensions and the sizes of the drops, thus gravity, fluid motion and the forces between particles are ignored.[23] When two immiscible drops come into contact, one drop can completely engulf the other drop only if the total interfacial energies are reduced. For the case illustrated in Fig. 1a1–a3, drop A (radius R_A) completely engulfs drop B (radius R_B), and the relationship of the interfacial energies fits in with eqn (1):

$$4\pi R_A{}^2 \gamma_{AC} + 4\pi R_B{}^2 \gamma_{BC} > 4\pi R_B{}^2 \gamma_{AB} + 4\pi \left(R_A{}^3 + R_B{}^3\right)^{\frac{2}{3}} \gamma_{AC} \quad (1)$$

where γ_{ij} is the interfacial tension between fluids i and j, and R_i is the radius of drop i.
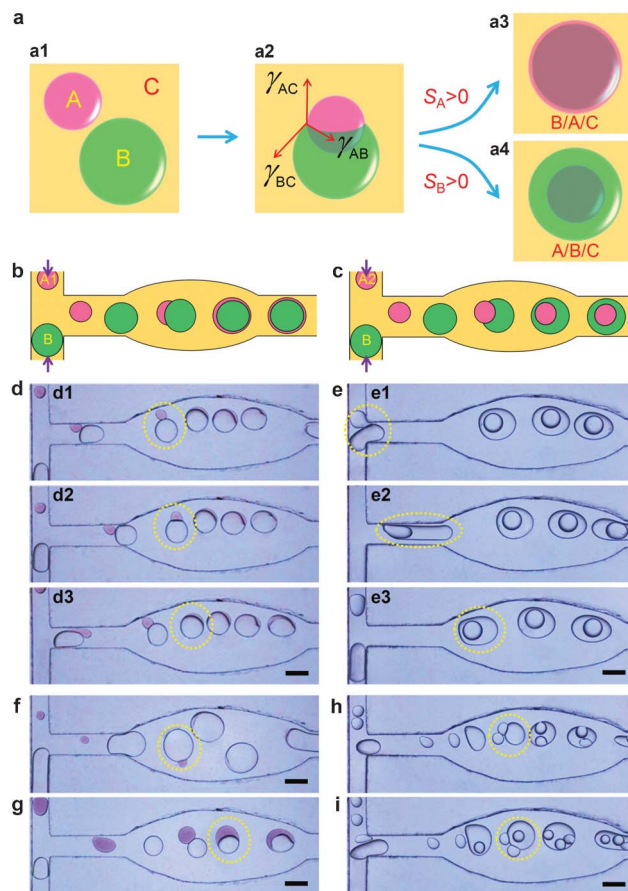
Eqn (1) can be deformed as:

$$\gamma_{BC} - (\alpha \gamma_{AC} + \gamma_{AB}) > 0 \quad (2)$$

where

$$\alpha = \left[1 + \left(\frac{R_A}{R_B}\right)^3\right]^{\frac{2}{3}} - \left(\frac{R_A}{R_B}\right)^2, \alpha \in (0,1) \quad (3)$$

The spreading coefficient is defined as:

$$S_A = \gamma_{BC} - (\alpha \gamma_{AC} + \gamma_{AB}) \quad (4)$$

Fig. 1 Wetting-induced formation of double emulsions. (a) Schematic of the wetting-induced engulfing process of two immiscible drops (A and B) in a third fluid (C), which is controlled by adjusting the interfacial energies. (b–e) Schematics and high-speed snapshots of wetting-induced formation of double emulsions, in which water drops (B) are completely engulfed by oil drops (A1, dyed with LR300) to form B/A1/C double emulsions (b, d), or water drops (B) totally engulf oil drops (A2) to form A2/B/C double emulsions (c, e). (f–i) High-speed snapshots of the engulfing formation of B/A1/C double emulsions with an ultra-thin shell (f) and a relatively thick shell (g) as well as A2/B/C double emulsions with two (h) or three (i) inner drops. Scale bars, 200 μm.

As a consequence, full engulfment requires a positive spreading coefficient ($S_A > 0$), which implies that the fluid of the engulfing drop A preferentially wets the interface of the engulfed drop B compared to the continuous fluid C. Similarly, if the interfacial energies are changed to make S_B positive, drop B will completely engulf drop A to form an A/B/C double emulsion, as shown in Fig. 1a2, a4. This method of making multiple emulsions requires three kinds of immiscible liquids. Those oil phases that are immiscible with many other kinds of oil and water phases, for example, the silicone oil series and the fluorinated oil series, especially the commonly-used fluorocarbon oils, can be used as the continuous phases. By adding surfactants or other reagents to the systems or by controlling the sizes of the drops, the interfacial energies can be simply adjusted to make different spreading coefficients, which allows us to create diverse structures of multiple emulsions. Control of the spreading coefficients of immiscible

phases has been used to create a wide variety of shapes by causing partial wetting of the interface.[24-26] Here we ensure that the wetting of immiscible drops is complete, causing the outer drop to fully engulf the inner drop to form a multiple emulsion.

Experimental

Materials

To prepare multiple emulsion drops, soybean oil (SO) (Tieling Beiya Pharmaceutical Oils) or a mixture of SO and octanol (3 : 1, v/v) containing 1–2 wt.% polyglycerol polyricinoleate (PGPR 90), an aqueous solution containing 0.5–1 wt.% sodium dodecyl sulfate (SDS), and silicone oil (SiO) (10 cSt, Jinan Yingchuang Chemicals) containing 0.5–1 wt.% Dow Corning 749 (DC749) (Dow Corning Corporation) are employed as the immiscible phases. Trimethylolpropane ethoxylate triacrylate (ETPTA) (average $M_n \sim 692$, Sigma-Aldrich) containing 1 vol.% photoinitiator 2-hydroxy-2-methylpropiophenone (Sigma-Aldrich) is used as the middle oil phase of water-in-oil-in-oil (W/O/O) double emulsions to fabricate microcapsules with different shells. The polymerization is initiated by UV for 5 min.

Set up and characterization

To perform the engulfing of the two immiscible drops, we designed a microfluidic device containing two flow-focusing drop generators and a common collection microchannel with an expanded chamber (Fig. 1b, c and S1a, ESI†). The microfluidic devices 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 connecting a glass tube and several syringe needles as the outlet and inlets with epoxy resin.[27] Syringes and syringe pumps (LSP01-1A, Baoding Longer Precision Pumps) are used for driving fluid flows into the microchannels. The formation and engulfing process of the drops are observed with an inverted optical microscope (IX71, Olympus) equipped with a high speed camera (Miro3, Phantom, Vision Research). The freshly prepared emulsions dyed with Lumogen® F Red 300 (LR300) (BASF) and fluorescein isothiocyanate (FITC) (Sigma-Aldrich) are observed with a confocal laser scanning microscope (CLSM) (SP5-II, Leica) with excitation at approximately 488 nm and 494 nm. The morphologies of dried ETPTA microcapsules are observed with a scanning electron microscope (SEM) (G2 Pro, Phenom). The interfacial tensions between immiscible phases are measured using a drop shape analysis system (DSA25, Krüss GmbH) at a temperature of 298 ± 1 K.

Results and discussion

### Wetting-induced formation of double emulsions

To demonstrate this new method of generating multiple emulsions, we utilize a glass microfluidic device[27] with two flow-focusing drop generators (Fig. S1a, ESI†) to create two different drops, of which one comprises of soybean oil (A1) and the second comprises of water (B), in a continuous phase of silicone oil (C). An expanded chamber (Fig. 1b, c) is designed in the collection microchannel of the microfluidic device to slow down the local flowrate of the drops and ensure contact between neighboring drops. To stabilize the drops before the engulfing, we add 1–2 wt.% PGPR 90 to the soybean oil and 0.5–1 wt.% SDS to the water as surfactants, and 0.5–1 wt.% DC749 to the silicone oil as a stabilizer. With this combination of surfactants and stabilizer, the interfacial tensions are $\gamma_{A1B} = 0.18$ mN m^{-1}, $\gamma_{BC} = 3.07$ mN m^{-1} and $\gamma_{A1C} = 1.37$ mN m^{-1}, and the spreading coefficient for the soybean oil over the water is always positive in spite of drop sizes ($S_{A1} > 1.52$, see ESI† Note Case 1 for details). Thus, when a soybean oil drop A1 meets a water drop B in the expanded chamber of the collection channel, the soybean oil drop A1 completely engulfs the water drop B, forming a B/A1/C water-in-oil-in-oil (W/O/O) double emulsion (Fig. 1d). This illustrates the principle of direct multiple-emulsion formation from two independent drops through control of wettability. This method has great flexibility and controllability. For example, by simply adding 25 vol.% octanol to the soybean oil (A2), the interfacial tensions are adjusted to $\gamma_{A2B} = 0.58$ mN m^{-1}, $\gamma_{BC} = 3.07$ mN m^{-1} and $\gamma_{A2C} = 3.16$ mN m^{-1}, which make the spreading coefficient of the water phase (B) over the soybean oil phase (A2) (S_B) positive if the drop size ratio of R_B/R_{A2} is larger than 0.49 (see ESI† Note Case 2 for details). Thus, the engulfing process can be inverted to form A2/B/C oil-in-water-in-oil (O/W/O) double emulsions (Fig. 1c, e). The thickness of the middle phase in double emulsions can be controlled by adjusting the relative size of the drops, to make, for example, core-shell structures with very thin shells (Fig. 1f, S1 and Movie S1, ESI†) or relatively thick shells (Fig. 1g). Alternatively, control of the size of multiple emulsions can also be achieved simply by adjusting the size of the precursor drops. In addition, the number of inner drops in double emulsions can be easily controlled by adjusting the number ratio of the drops that converge in the collection channel (Fig. 1h, i, S2 and Movie S2, ESI†). Moreover, we can also easily control the type of inner drops in double emulsions by using diverse disperse fluids, which is demonstrated by using a water drop to simultaneously engulf two different oil drops to form (O1+O2)/W/O emulsions with different inner drops (Fig. S3, ESI†).

Double emulsions with ultra-thin shells and resultant microcapsules

The ability to precisely control the formation of multiple emulsions offers new opportunities to engineer novel materials. To illustrate this potential, we use the double emulsions with ultra-thin shells as templates to fabricate ultra-thin shelled microcapsules. We prepare the W/O/O double emulsions with ultra-thin shells by spreading SO drops over water drops in SiO phase (Fig. S4, ESI†). The double emulsions have good monodispersity (Fig. 2a) and diverse structures (Fig. 2b–d and S5, ESI†). For the W/O/O double emulsions with ultra-thin shells in Fig. 2a, the mean diameter is 205.4 μm and the coefficient of variation is only 1.92%. Ultra-thin shelled emulsions with multiple inner drops show diverse configura-
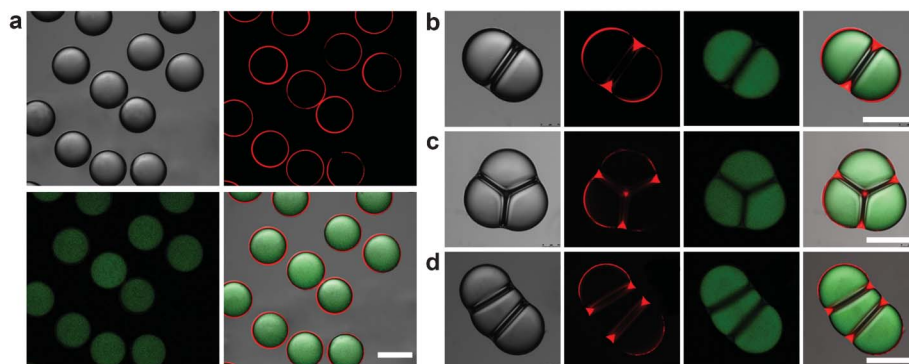
Fig. 2 Double emulsions with ultra-thin shells. (a–d) CLSM images of ultra-thin shelled W/O/O double emulsions containing one (a), two (b) or three (c, d) inner drops. Scale bars, 200 μm.

tions dependent on the assembly pattern of the inner drops. The ultra-thin shelled double emulsions with three inner drops display two different configurations, *i.e.*, triangular (Fig. 2c) and linear (Fig. 2d) configurations; while those with four inner drops display three different configurations, *i.e.*, linear, planar and tetrahedral configurations (Fig. S5, ESI†). Besides ultra-thin shells for the W/O/O double emulsions, adjustable shells for the double emulsions can also be achieved effectively (Fig. 3a–d). For a core-shell double emulsion, the shell thickness (δ) can be precisely controlled from the relationship between the δ and the diameters (D_1 for the engulfing drop and D_2 for the engulfed drop) of the precursor drops with an equation (Fig. 3a)

$$\delta = \left[\left(D_1^3 + D_2^3 \right)^{\frac{1}{3}} - D_2 \right] / 2 \qquad (5)$$
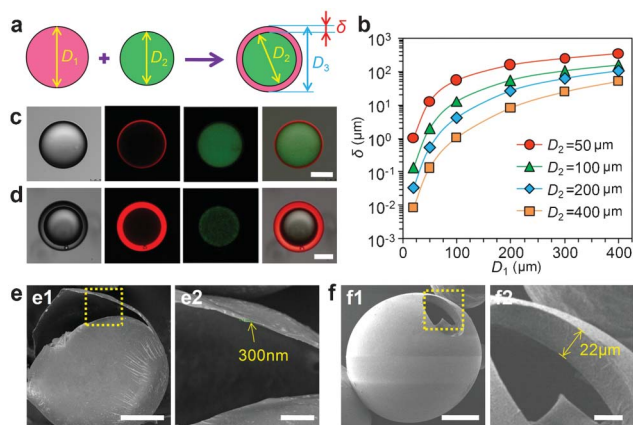
Fig. 3 Double emulsions with controllable shells and the as-prepared microcapsules. (a, b) The relationship between the shell thickness (δ) of the double emulsions and the diameters of the precursor drops (D_1, D_2), in which the shell volume of the double emulsion equals the volume of drop D_1. (c, d) CLSM images of double emulsions with ultra-thin shells (c) and relatively thick shells (d). (e, f) SEM images of the prepared ETPTA microcapsules with an ultra-thin shell (e) and a relatively thick shell (f), in which e2 and f2 are magnifications of the dashed areas in e1 and f1, respectively. Scale bars in c, d, e1 and f1 are 100 μm, and those in e2 and f2 are 20 μm.

If D_1 is fixed, δ decreases as D_2 increases; on the contrary, if D_2 is fixed, δ increases with increasing D_1. For example, when D_2 is 200 μm, δ increases from 33 nm to 26 μm when D_1 increases from 20 μm to 200 μm (Fig. 3b). As-prepared double emulsions with ultra-thin shells and relatively thick shells are shown in Fig. 3c and 3d, respectively. This enables efficient fabrication of microcapsules with a desired shell thickness, especially the ultra-thin shelled microcapsules. We demonstrate this by spreading photocurable ETPTA drops over the water drops to prepare core-shell microcapsules with controllable shell thicknesses. ETPTA microcapsules with an ultra-thin shell (δ = 300 nm for a capsule with an outer diameter of about 310 μm) (Fig. 3e) and a relatively thick shell (δ = 22 μm for a capsule with an outer diameter of about 350 μm) (Fig. 3f) are prepared by changing the size of the precursor ETPTA drops.
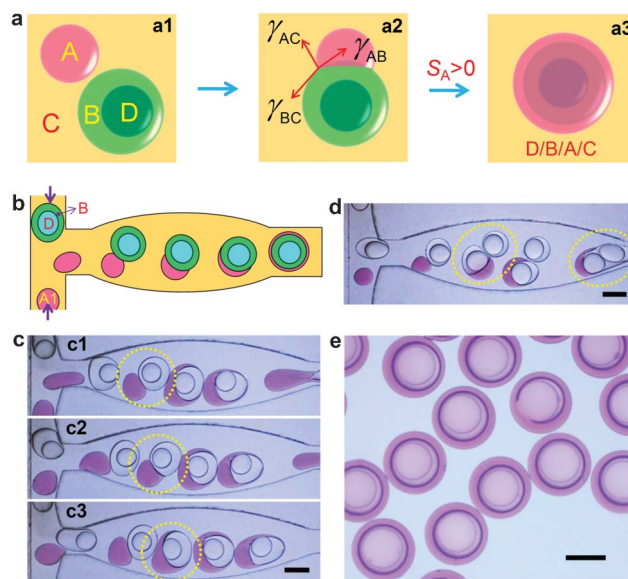
Wetting-induced formation of higher-order multiple emulsions

This wetting-induced drop-engulfing-drop method for fabricating multiple emulsions has a significant advantage that it can be very easily scalable to higher-order multiple emulsions. We illustrate this concept by fabricating monodisperse O/W/O double emulsions with diverse inner oil cores (Fig. 4), as well as monodisperse triple emulsions that consist of oil-in-water-in-oil-in-oil (O/W/O/O) drops (Fig. 5). This preparation is accomplished by spreading O/W/O double emulsion drops over O/O drops (Fig. 4a) or in the reverse way (Fig. 5a). Both single-stage and double-stage flow-focusing drop generators are designed in the microfluidic device to generate single emulsions and double emulsions simultaneously (Fig. 4b). To create (A+D)/B/C ((O1+O2)/W/O) double emulsions with two different inner oil cores (Fig. 4a3, b), SiO containing 1 wt.% DC749 is employed as the continuous phase (C) in both generators, an aqueous solution containing 1 wt.% SDS and SO with 1 wt.% PGPR 90 are respectively used as the middle phase (B) and inner phase (D) in the double-stage drop generator to create D/B/C (O/W/O) emulsions (Fig. 4c), and a mixture of SO and octanol (3 : 1, v/v) containing 1 wt.% PGPR 90 and 1 mg mL^{-1} LR 300 is used as the disperse phase (A2) in the single-stage drop generator to prepare A2/C (O/O) emulsions (Fig. 4d). This fluid combination makes a positive
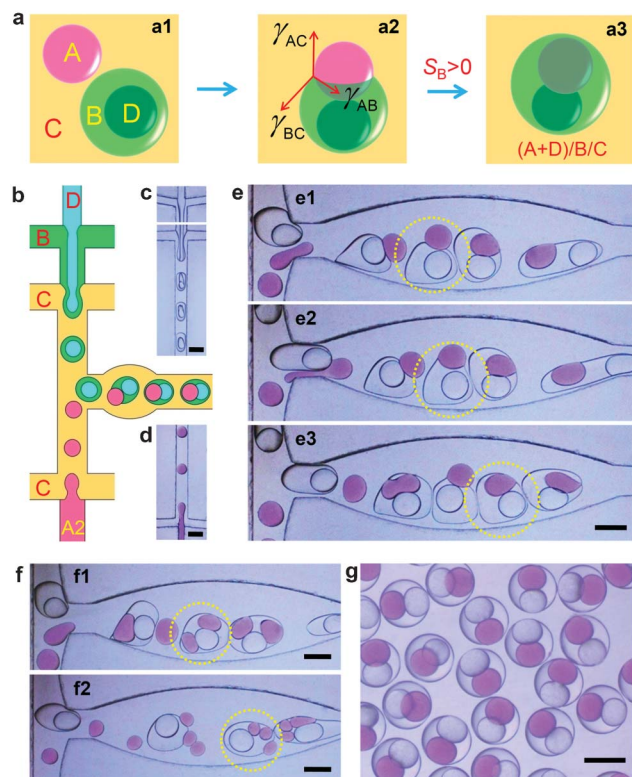
Fig. 4 Wetting-induced formation of double emulsions containing different inner drops. (a) Schematic of wetting-induced complete engulfing of one O/O single emulsion drop by one O/W/O double emulsion drop to form an (A2+D)/B/C double emulsion containing different inner drops when the spreading coefficient S_B is positive. (b–e) Schematic and high-speed optical micrographs of the preparation of precursor drops (c, d) and double emulsions containing two different inner drops (e). (f) One O/W/O double emulsion drop completely engulfs two or three precursor O/O single emulsion drops to form an (O1+O2+O2)/W/O (f1) or an (O1+O2+O2+O2)/W/O (f2) multiple emulsion, respectively. (g) Optical micrograph of the as-prepared monodisperse double emulsions containing two different inner drops. Scale bars, 200 μm.

Fig. 5 Wetting-induced formation of triple emulsions. (a) Schematic of wetting-induced complete engulfing of one O/W/O double emulsion drop by one O/O single emulsion drop to form a D/B/A1/C triple emulsion when the spreading coefficient S_A is positive. (b, c) Schematic and high-speed optical micrographs of the preparation of triple emulsions. (d) One O/O single emulsion drop completely engulfs two O/W/O double emulsion drops to form an O/W/O/O triple emulsion with two double emulsion drops as cores. (e) Optical micrograph of the as-prepared monodisperse triple emulsions. Scale bars, 200 μm.

spreading coefficient for the phase B over the phase A. Therefore, as pairs of the single emulsion drop and the double emulsion drop meet in the expanded chamber, the water shell of the D/B/C double emulsion drop completely spreads over the A2/C single emulsion drop to form (A2+D)/B/C (O1+O2)/W/O double emulsions (Fig. 4e, and Movie S3, ESI†). The reverse engulfing process can be achieved by changing the disperse oil phase of the A/C single emulsion to enable a positive spreading coefficient of the phase A over the phase B (Fig. 5a3). We demonstrate this by using SO containing 2 wt.% PGPR 90 and 1 mg mL^{-1} LR 300 as the disperse phase (A1) of the A/C single emulsion to completely engulf the D/B/C double emulsion drop, directly forming D/B/A1/C oil-in-water-in-oil-in-oil (O/W/O/O) triple emulsions (Fig. 5b, c, and Movie S3, ESI†). The prepared (O1+O2)/W/O double emulsions and O/W/O/O triple emulsions show excellent monodispersity and high stability (Fig. 4g, 5e). By changing the fluids and adjusting the interface energies, the flexibility of this approach enables us to prepare (W1+W2)/O/O double emulsions and W/

O/W/O triple emulsions *via* the engulfing of W/O/O double emulsions and W/O single emulsions.

The simplicity of this method also enables us to generate multiple emulsions with more complex structures. For example, we can create multiple emulsions with a controllable number of either inner single emulsion drops (Fig. 4f and S6, ESI†) or inner double emulsion drops (Fig. 5d and S7, ESI†) by simply adjusting the number ratio of the emulsion drops that converge in the collection channel. These multi-core emulsions would offer advanced platforms for the design of more complex multi-compartment materials, and provide synergistic delivery systems for incompatible actives with more precise encapsulation.

Conclusions

In summary, we have demonstrated a qualitatively novel approach for creating highly controlled monodisperse multiple emulsions through simply putting individual immiscible drops together. The multiple emulsions are directly formed in microchannels from wetting-induced drop-engulfing-drop phenomena by carefully controlling the interfacial energies. Our approach exhibits exceptionally controllable flexibility and provides a valuable concept to prepare multiple emulsions. We demonstrate these in preparation of both double and triple emulsions with a controlled number of inner drops including both single and double emulsion drops, and with precisely adjusted shell thicknesses including ultra-thin shells. Such a

controllable wetting-induced drop-engulfing-drop approach in microfluidics makes it an ideal method to precisely manipulate small volumes of fluids for further investigations and applications of microfluidics.[28] Furthermore, this innovative approach opens a window to discover and exploit new phenomena occurring in fluids at the microscale level, which is of great significance for developing novel microfluidics and will be a fertile area of research.

Acknowledgements

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