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SHORT COMMUNICATION

Multiple emulsion formation from controllable drop pairs in microfluidics

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Abstract A novel and reliable approach is developed for generating highly controlled multiple emulsions from controllable drop pairs in microfluidics. Drop pairs are accurately generated by drop-triggered drop formation and precise drop-pairing, and then one drop completely engulfs the other immiscible drop to form a multiple emulsion by adjusting their interfacial energies. This approach successfully avoids the complex sequential emulsifications and shows great stability and controllable flexibility. In addition, our strategy for drop-pairing is so reliable that it allows long-term operation without any misorder at all. Importantly, the proposed method of drop-pairing and multiple emulsion formation provides an innovative platform to precisely manipulate small volumes of fluids, which is of great value for exploiting novel microfluidics.

Keywords Multiple emulsions · Drop-pairing · Microfluidics · Drop-engulfing-drop · Interfaces

1 Introduction

Multiple emulsions are complex nested systems of drops, in which drops of one fluid containing smaller drops of a second fluid are dispersed in a third immiscible fluid. They have significant potential in myriad applications, including foods (Muschiolik 2007; McClements and Li 2010), cosmetics (Lee et al. 2001), drop networks (Villar et al. 2011), controlled microreactors (Duncanson et al. 2012; Theberge et al. 2010), synthesis of microcapsules (Shum et al. 2011; Chu et al. 2007; Liu et al. 2010), drug delivery systems (Engel et al. 1968; Nakano 2000). Multiple emulsions are typically formed by multi-step sequential drop-formation and drop-encapsulation of a succession of bulk emulsifications using shear cells or porous membrane plates (Joscelyne and Trägårdh 2000; van der Graaf et al. 2005; Goubault et al. 2001). Owing to the randomicity of each emulsification, the conventional methods usually result in polydisperse structures including broad size distributions and poorly controlled morphologies. Recent advances in microfluidic techniques provide a flexible platform for generating multiple emulsions that possess perfect monodispersity and diverse structures (Utada et al. 2005; Wang et al. 2011; Okushima et al. 2004; Seo et al. 2007). However, the multi-step sequential emulsifications in microfluidics crucially rely on larger-scale devices, such as multi-stage tailored poly(dimethylsiloxane) (PDMS) devices (Abate and Weitz 2009) or assembled glass capillary devices (Chu et al. 2007; Wang et al. 2011), which are either difficult to fabricate or complicated to spatially pattern the surface wettability of microchannels. Besides, skilled and sophisticated control of flows at each stage is also quite essential to obtain the stable sequential emulsification processes. Kim and Weitz reported a one-step emulsification method to make multiple emulsions of high

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order from multiple coaxial interfaces by using a relatively simple capillary device (Kim and Weitz 2011), whereas it has difficulty in controlling the interior morphologies of multiple emulsions, for example, the number of inner cores, and the stable multiple coaxial interfaces are also complicated to achieve. Recently, we have reported a simplified method for generating highly controlled multiple emulsions from wetting-induced drop-engulfing-drop phenomena (Deng et al. 2013), which successfully evades the complex sequential emulsification processes. This method requires precise drop-pairing for controllable production of multiple emulsions. Although drop pairs can be formed by adjusting flow rates with high accuracy equipments, it is still challenging for long-term operations because of the relatively poor ability of equipments to resist environmental interference.

In this paper, we present a robust approach for generating highly controlled multiple emulsions from controllable drop pairs in microfluidics. Firstly, drop pairs are accurately generated by drop-triggered drop formation and precisely drop-pairing. And then, by carefully controlling the interfacial energies, one drop can completely engulf the other immiscible drop to form a multiple emulsion directly (Deng et al. 2013). Compared with established microfluidics for multiple emulsions, our method proposed here does not require complex control of flows at each stage. We divide the multi-stage process of emulsification into two simpler processes or more, and then make multiple emulsions from the simply formed, lower-order drop pairs in microchannels by drop-engulfing-drop. This approach of generating multiple emulsions from controllable drop pairs in microfluidics shows high stability and controllable flexibility. Moreover, the proposed drop-pairing strategy is also highly potential in preparation of emulsions from high-viscosity fluids and in drop-coalescence-triggered micro-reactions.

2 Materials and methods

2.1 Materials

To prepare multiple emulsions, three immiscible phases are selected as follows. (1) Outer continuous oil phase is silicone oil (SiO) (10 cSt) containing 1 % (w/v) Dow Corning 749 (DC749, which is a mixture of approximately 50 % decamethylcyclopentasiloxane and 50 % trimethylated silica, commercially from Dow Corning); 2) Inner aqueous phase is water containing 1 % (w/v) sodium dodecyl sulfate (SDS); 3) Inner oil phase is soybean oil (SO) containing 2 % (w/v) polyglycerol polyricinoleate (PGPR 90, commercially from Danisco) for preparing water-in-oil-in-oil (W/O/O) double emulsions, while it is a mixture of SO and octanol (3:1, v/v) containing 2 % (w/v) PGPR 90 for preparing oil-in-water-in-oil (O/W/O) double emulsions. DC749 is used as a stabilizer in silicone oil to prevent undesired coalescence of drops, and it can reduce the interfacial tension between SiO and water and that between SiO and SO to certain extents. PGPR90 is used as a surfactant in SO, and it can significantly reduce the interfacial tension between SO and water, but has a negligible impact on the interfacial tension between SiO and SO. SDS is used as a water-soluble surfactant to adjust the interfacial energies and to stabilize the droplets against undesired coalescence.

2.2 Setup and characterization

The microfluidic devices are fabricated by bonding patterned coverslips (thickness of 130–170 μm) into a microscope glass slide in designed geometries with a UV-curable adhesive, and connected with a glass tube and several syringe needles as outlet and inlets by epoxy resin (Deng et al. 2011). The surface wettability properties of microchannels in our devices can be easily modified spatially by self-assembled monolayer chemistry and flow confinement method, which has been reported in our previous paper (Deng et al. 2011). Syringes and syringe pumps (LSP01-1A, Baoding Longer Precision Pumps) are utilized to drive fluids into the microfluidic devices. The preparation processes of multiple emulsions are observed by an inverted optical microscope (IX71, Olympus) equipped with a high-speed camera (Miro3, Phantom, Vision Research). The prepared multiple emulsions containing dye Lumogen® F Red 300 (LR300) (BASF) are observed by a confocal laser scanning microscope (CLSM, SP5-II, Leica) with excitation at approximate 488 nm. The interfacial tensions between immiscible phases are measured using a drop shape analysis system (DSA25, Krüss GmbH) at a temperature of 25 ± 1 °C.

3 Results and discussion

3.1 Preparation of drop pairs from drop-triggered drop formation and precise drop-pairing

To generate pairs of precursor drops of immiscible fluids from drop-triggered drop formation and precise drop-pairing, we employ a glass microfluidic device with two hydrophobic flow-focusing generators (Fig. 1a) to generate oil jets (Fig. 1b) and water drops (Fig. 1c) synchronously, in which the jets comprise of soybean oil (A) and the drops comprise of deionized water (B), in a continuous phase of silicone oil (C). An expanded chamber (Fig. 1a) is designed in the collection microchannel to slow down the local flow rates and assist the pairing of neighboring drops. As water drops and oil jets flow into the collection

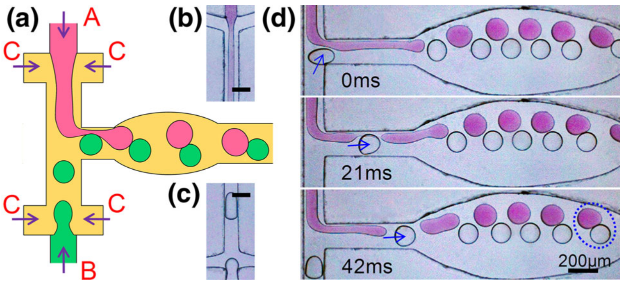

Fig. 1 Drop-triggered formation of drops for exact drop-pairing in microchannels. **a** A schematic of preparation of drop pairs from drop-triggered drop formation. **b–d** High-speed snapshots of the preparation of O/O jets (**b**) and W/O emulsion drops (**c**), as well as drop-triggered formation of drops for drop-pairing (**d**). The flow rates are: $Q_{\mathrm{A}} = 300\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 300\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 300\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 500\ \mu\mathrm{L\ h}^{-1}$. *Scale bars* are 200 μm

microchannel, the fluids of oil jets between consecutive water drops are sequentially sheared into oil drops, directly forming one-to-one drop pairs in the expanded chamber (Fig. 1d). The chamber also has an impact on the spreading and engulfing processes, but it does not decide the final equilibrium states and the stability of the emulsions formed. In the chamber, flowing condition is different from other channels, which causes the drop shapes and the interfacial tensions of the systems changed considerably to influence the drop-engulfing. The size of oil drops can be controlled not only by adjusting the flow rates in the generator of oil jets, but also by controlling the spacing between water drops. The shear-formed oil drops have excellent monodispersity (Fig. 1d). The method for preparing drop pairs we used here is by taking advantage of drop-triggered drop formation. It is very efficient and robust, and more resistant to environmental interference. Importantly, this method for drop-pairing is so reliable that it allows long-term operation without any misorder at all. In principle, this drop-triggered formation of drops in microchannels can be performed as long as we want till the solutions in syringes are used out. Usually, our experiments of drop-pairing are operated for about 8 h a day. Furthermore, this mechanism is competent to produce monodisperse emulsions from high-viscosity fluids that are difficult to achieve a stable dripping regime to generate monodisperse emulsions in the conventional sequential emulsification processes. For example, in 2011, Abate and Weitz presented a similar method of air-bubble-triggered drop formation to prepare double emulsions from jetting at a high speed in microfluidics (Abate and Weitz 2011).

3.2 Drop-triggered drop-pairing for preparing double emulsions

On the basis of the controlled drop-pairing, we adjust the interfacial energies of the immiscible phases by adding 2 % (w/v) PGPR 90 and 1 % (w/v) SDS to the soybean oil phase and the water phase as surfactants, respectively, and 1 % (w/v) DC749 to the silicone oil as stabilizer. With this combination of surfactants and stabilizer, the interfacial tensions are, respectively, $\gamma_{\mathrm{AB}} = 0.28\ \mathrm{mN\ m}^{-1}$, $\gamma_{\mathrm{BC}} = 8.82\ \mathrm{mN\ m}^{-1}$ and $\gamma_{\mathrm{AC}} = 1.21\ \mathrm{mN\ m}^{-1}$, and the spreading coefficient for the oil drop over the water drop is always positive ($S_{\mathrm{A}} = 7.33$, for which please see our published paper (Deng et al. 2013) for the calculation equations of the spreading coefficient). When there is no surfactants and stabilizer in the three fluids, the interfacial tensions are, respectively, $\gamma_{\mathrm{AB}} = 31.13\ \mathrm{mN\ m}^{-1}$, $\gamma_{\mathrm{BC}} = 50.33\ \mathrm{mN\ m}^{-1}$ and $\gamma_{\mathrm{AC}} = 2.43\ \mathrm{mN\ m}^{-1}$. Because of undesired coalescence of the same kind of drops, we do not carry out the drop-engulfing in the combination of the three phases without surfactants and stabilizer. As a pair of water drop (B) and soybean oil drop (A) contacts in the expanded chamber, the water drop B is entirely engulfed by the oil drop A to form a B/A/C W/O/O double emulsion (Figs. 2a–f; Supplementary Movie S1). The drop-pairing and the direction of their engulfment are decided by the relative flow rates of drops in the expanded chamber. When the flow rates of phases A and B are almost the same, the engulfing of the two drops performs perpendicularly to the flow direction (Fig. 2a, b). As the flowrate of oil jets is faster than that of the water drops, the shear-formed oil drops engulf the water drops ahead of them (Fig. 2c, d). When the flowrate of oil jets is slower than that of the water drops, the shear-formed oil drops engulf the water drops behind them (Fig. 2e, f). All of the three types of drop-pairing and drop-engulfing are highly stable for preparing double emulsions with good monodispersity, as shown in Fig. 2g. The preparation rate of drop pairs relies on the speed of preparation of water drops that are used to cut the oil jetting. Thereby, the rate of preparation of drop pairs can be as high as several hundred to thousand per second. However, the drop-engulfing in the expanded chamber requires relatively longer time, typically, tens of milliseconds; thus, the drop-engulfing is usually carried out at the speed of 20 s^{-1} or less. Compared with our previous work of forming drop pairs by carefully adjusting flow rates (Deng et al. 2013), the method of drop-triggered drop formation and precise pairing of drops in this study is much more efficient and robust, and more resistant to environmental interference. Importantly, the method presented here allows long-time manipulation.

This method has great flexibility and controllability. For example, we can easily invert the engulfing process by adjusting the spreading coefficient of the water phase over the soybean oil phase positive via simply adding 25 % (v/v) octanol to the soybean oil (Deng et al. 2013). Thus, the water drops can fully wet the oil drops, forming A/B/C O/W/O double emulsions (Fig. 3a, b). This method of drop-pairing and drop-engulfing also enables us to fabricate multiple emulsions with more complex structures. For example, we can generate multiple emulsions with different

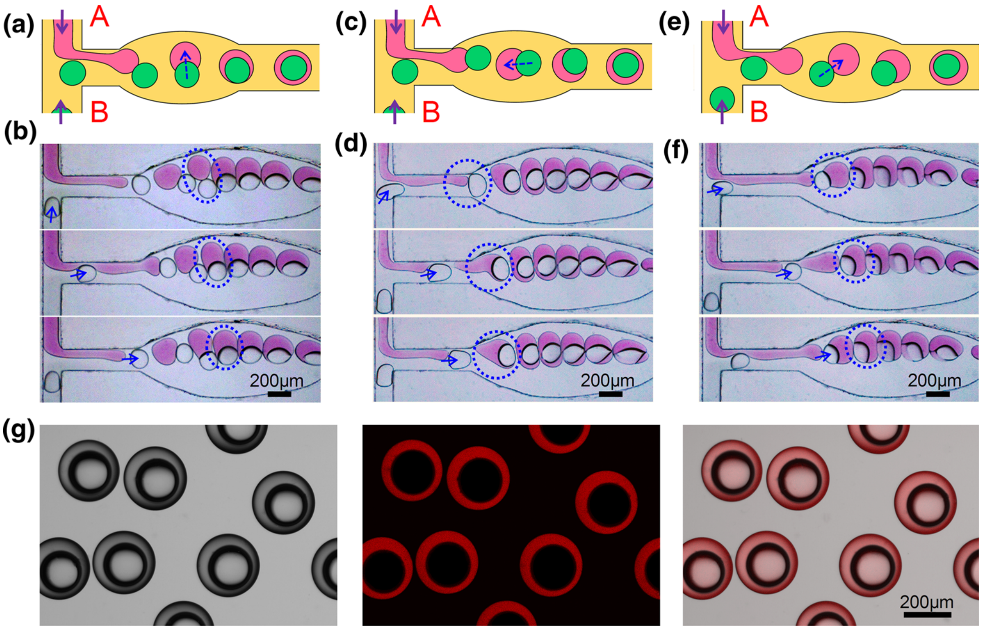

Fig. 2 Drop-triggered drop-pairing for preparing W/O/O double emulsions. **a**–**f** Schematics and high-speed snapshots of drop-triggered drop-pairing for preparing W/O/O double emulsions, in which oil jets (*A*) are cut by water drops (*B*) to form oil drops, and then the shear-formed oil drops completely engulf water drops to generate W/O/O double emulsions. Phase *A* is dyed with LR300. **a**, **b** The flow rates of phases *A* and *B* are almost the same, **c**, **d** the flowrate of phase *A* is faster than that of phase *B*, and **e**, **f** the flowrate of phase *A* is slower than that of phase *B*. **g** CLSM images of the as-prepared W/O/O double emulsions. The schematic of the microfluidic device is the same as Fig. 1a. The flow rates for case **b** are: $Q_{\mathrm{A}} = 300\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 200\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 300\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 500\ \mu\mathrm{L\ h}^{-1}$; those for case **d** are: $Q_{\mathrm{A}} = 200\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 200\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 100\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 300\ \mu\mathrm{L\ h}^{-1}$; and those for case **f** are: $Q_{\mathrm{A}} = 200\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 200\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 200\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 500\ \mu\mathrm{L\ h}^{-1}$. *Scale bars* are 200 μm

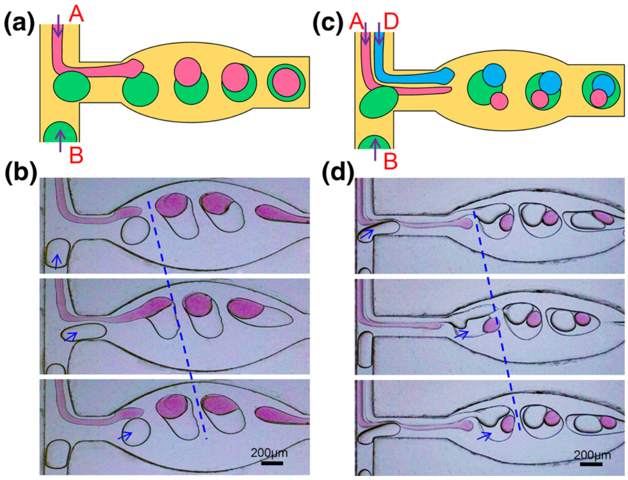

Fig. 3 Schematics and high-speed snapshots of the engulfing of water drops over oil drops to generate O/W/O double emulsions with one inner drop (**a**, **b**) or two different inner drops (**c**, **d**). The schematic of the microfluidic device is the same as Fig. 1a. **c** We inject phases *A* and *D* into the side channels as well as phase *C* into the center channel of the upper generator. The flow rates for case **b** are: $Q_{\mathrm{A}} = 350\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 300\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 300\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 600\ \mu\mathrm{L\ h}^{-1}$; and those for case **d** are: $Q_{\mathrm{A}} = 20\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{D}} = 20\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{C(upper)}} = 100\ \mu\mathrm{L\ h}^{-1}$, $Q_{\mathrm{B}} = 150\ \mu\mathrm{L\ h}^{-1}$ and $Q_{\mathrm{C(lower)}} = 400\ \mu\mathrm{L\ h}^{-1}$. *Scale bars* are 200 μm

inner drops by simply adjusting the number of the disperse phases that make jets in one generator. As Fig. 3c, d shown, we demonstrate this by preparing O/W/O emulsions with two different interior drops [(O1 + O2)/W/O] through adding SO and octanol (3:1, v/v) with 2 % (w/v) PGPR 90 as another disperse oil phase. The two oil jets are sheared by one water drop simultaneously to make two different oil drops, forming a one-to-two drop pair. Then, the water drop completely engulfs the two oil drops to generate an (O1 + O2)/W/O double emulsion. Similarly, double emulsions containing more complex components can be generated by applying more disperse oil phases. These emulsions have a great potential in preparations of multi-compartment materials and synergistic delivery systems.

3.3 Drop-triggered drop-pairing for preparing triple emulsions

The proposed method of drop-pairing and drop-engulfing is easily scalable to higher-order multiple emulsions. We illustrate this concept by pairing single emulsion drops and double emulsion drops for fabricating monodisperse oil-in-water-in-oil-in-oil (O/W/O/O) triple emulsions (Fig. 4a).

Generally, triple emulsions are generated via three-step sequential emulsifications in microfluidics. Here, we divide the complex process into two relatively simple emulsifications. Both single-stage and double-stage flow-focusing generators are designed in the microfluidic device to generate oil jets and double emulsions simultaneously. To fabricate O/W/O emulsions in double-stage flow-focusing generators, we pattern the first and the second junctions of the double-stage generator to be hydrophilic and hydrophobic, respectively, and the rest of channels are hydrophobic by self-assembled monolayer chemistry and flow confinement method (Deng et al. 2011). To generate O/W/O/O triple emulsions, SiO containing 1 % (w/v) DC749 is employed as continuous phase (C) in both generators, aqueous solution containing 1 % (w/v) SDS and SO with 2 % (w/v) PGPR 90 are, respectively, used as middle phase (B) and inner phase (D) in the double-stage drop generator to generate D/B/C (O/W/O) emulsions (Fig. 4b), and SO containing 2 % (w/v) PGPR 90 and 1 mg mL^{-1} LR 300 is used as disperse phase (A) in the single-stage generator to prepare A/C (O/O) jets (Fig. 4c). This fluid combination makes a positive spreading coefficient for the phase A over the phase B. The fluids of phase A between consecutive O/W/O double emulsions become drops, directly forming one-to-one drop pairs in the expanded chamber. Similarly, as pairs of the single emulsion drop and the double emulsion drop contact, the O/O single emulsion drops completely engulf the O/W/O double emulsion drops, forming O/W/O/O triple emulsions (Fig. 4d; Supplementary Movie S2). The as-prepared O/W/O/O triple emulsions show excellent monodispersity and high stability (Fig. 4e). For the triple emulsions shown in Fig. 4e, the mean diameters of inner drops, middle drops and outer drops are 198.1 µm, 238.4 µm and 310.1 µm, respectively, and their coefficient of variation (CV) values are as small as 4.2 %, 2.8 % and 1.7 %, respectively. The coefficient of variation (CV) value is define as the ratio of the standard deviation of size distribution to its arithmetic mean, and calculated with an equation $\mathrm{CV} = \frac{1}{\bar{d}}\left[\sum_{i=1}^{n}(d_i - \bar{d})^2/n-1\right]^{1/2} \times 100\,\%$, in which d_i is the diameter of the ith drop, $\bar{d}$ is the arithmetic average diameter and n is the number of drops measured.

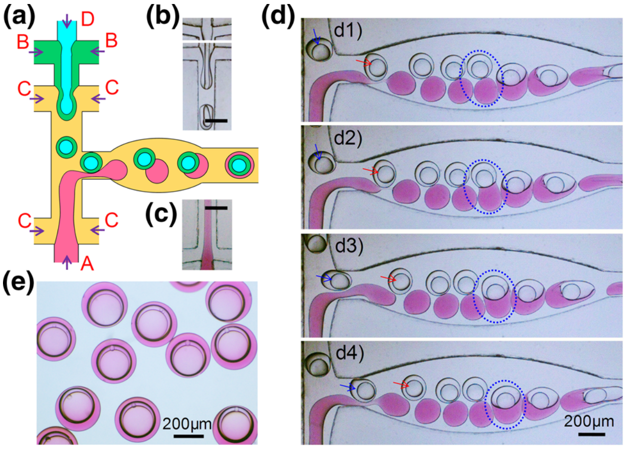

Fig. 4 Wetting-induced formation of O/W/O/O triple emulsions from pairs of O/O single emulsion drops and O/W/O double emulsion drops. **a**–**d** A schematic and high-speed snapshots of preparation of O/W/O emulsions (**a**, **b**) and O/O jets (**a**, **c**) as well as drop-triggered drop-pairing for preparing O/W/O/O triple emulsions (**d**), in which oil jets (*A*) are sheared by O/W/O double emulsion drops (*B*) to form oil drops, and then the oil drops completely engulf the O/W/O emulsion drops to generate O/W/O/O triple emulsions. **e** Optical micrograph of the as-prepared O/W/O/O triple emulsions. The flow rates are: $Q_{\mathrm{A}} = 500$ µL h^{-1}, $Q_{\mathrm{C(lower)}} = 300$ µL h^{-1}, $Q_{\mathrm{D}} = 250$ µL h^{-1}, $Q_{\mathrm{B}} = 150$ µL h^{-1} and $Q_{\mathrm{C(upper)}} = 500$ µL h^{-1}. *Scale bars* are 200 µm

4 Conclusions

In summary, we have developed a simplified and robust method to make multiple emulsions from controllable drop pairs that are accurately generated from drop-triggered drop formation and precisely drop-pairing. The fluids of oil jets between consecutive water drops are sequentially sheared into oil drops, thereby directly forming one-to-one drop pairs. By simply adjusting the interfacial energies, one drop can totally engulf the other drop to form a multiple emulsion directly. This method exhibits high stability and controllable flexibility. By adjusting spreading coefficients, the complete engulfing between two immiscible drops (A and B) can be performed in two opposite manners, i.e., A-engulfing-B or B-engulfing-A. In addition, the proposed drop-pairing method is so reliable that it allows long-term operation without any misorder at all, and it has a high potential in drop-based microreactors that require accurate drop-pairing. Moreover, this drop-triggered drop formation method is also competent to produce monodisperse emulsions from high-viscosity fluids. Consequently, the proposed method for both drop-pairing and multiple emulsion formation offers an innovative platform to precisely manipulate small volumes of fluids, which is of great value for developing novel microfluidics.

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References

Abate AR, Weitz DA (2009) High-order multiple emulsions formed in poly(dimethylsiloxane) microfluidics. Small 5(18):2030–2032. doi:10.1002/smll.200900569

Abate AR, Weitz DA (2011) Air-bubble-triggered drop formation in microfluidics. Lab Chip 11(10):1713–1716. doi:10.1039/c1lc20108e

Chu L-Y, Utada AS, Shah RK, Kim J-W, Weitz DA (2007) Controllable monodisperse multiple emulsions. Angew Chem Int Ed 46(47):8970–8974. doi:10.1002/anie.200701358

Deng N-N, Meng Z-J, Xie R, Ju X-J, Mou C-L, Wang W, Chu L-Y (2011) Simple and cheap microfluidic devices for the preparation of monodisperse emulsions. Lab Chip 11(23):3963–3969. doi:10.1039/C1LC20629J

Deng N–N, Wang W, Ju X-J, Xie R, Weitz DA, Chu L-Y (2013) Wetting-induced formation of controllable monodisperse multiple emulsions in microfluidics. Lab Chip 13(20):4047–4052. doi:10.1039/C3LC50638J

Duncanson WJ, Abbaspourrad A, Shum HC, Kim SH, Adams LL, Weitz DA (2012) Monodisperse gas-filled microparticles from reactions in double emulsions. Langmuir 28(17):6742–6745. doi:10.1021/la300915p

Engel RH, Riggi SJ, Fahrenbach MJ (1968) Insulin: intestinal absorption as water-in-oil-in-water emulsions. Nature 219(5156): 856–857. doi:10.1038/219856a0

Goubault C, Pays K, Olea D, Gorria P, Bibette J, Schmitt V, Leal-Calderon F (2001) Shear rupturing of complex fluids: application to the preparation of quasi-monodisperse water-in-oil-in-water double emulsions. Langmuir 17(17):5184–5188. doi:10.1021/la010407x

Joscelyne SM, Trägårdh G (2000) Membrane emulsification—a literature review. J Membr Sci 169(1):107–117. doi:10.1016/S0376-7388(99)00334-8

Kim S-H, Weitz DA (2011) One-step emulsification of multiple concentric shells with capillary microfluidic devices. Angew Chem Int Ed 123(37):8890–8893. doi:10.1002/ange.201102946

Lee M-H, Oh S-G, Moon S-K, Bae S-Y (2001) Preparation of silica particles encapsulating retinol using O/W/O multiple emulsions. J Colloid Interface Sci 240(1):83–89. doi:10.1006/jcis.2001.7699

Liu L, Wang W, Ju X-J, Xie R, Chu L-Y (2010) Smart thermo-triggered squirting capsules for nanoparticle delivery. Soft Matter 6(16):3759–3763. doi:10.1039/C002231D

McClements DJ, Li Y (2010) Structured emulsion-based delivery systems: controlling the digestion and release of lipophilic food components. Adv Colloid Interface Sci 159(2):213–228. doi:10.1016/j.cis.2010.06.010

Muschiolik G (2007) Multiple emulsions for food use. Curr Opin Colloid Interface Sci 12(4–5):213–220. doi:10.1016/j.cocis.2007.07.006

Nakano M (2000) Places of emulsions in drug delivery. Adv Drug Deliver Rev 45(1):1. doi:10.1016/S0169-409X(00)00096-X

Okushima S, Nisisako T, Torii T, Higuchi T (2004) Controlled production of monodisperse double emulsions by two-step droplet breakup in microfluidic devices. Langmuir 20(23): 9905–9908. doi:10.1021/la0480336

Seo M, Paquet C, Nie Z, Xu S, Kumacheva E (2007) Microfluidic consecutive flow-focusing droplet generators. Soft Matter 3(8):986–992. doi:10.1039/B700687J

Shum HC, Y-j Zhao, Kim S-H, Weitz DA (2011) Multicompartment polymersomes from double emulsions. Angew Chem Int Ed 50(7):1648–1651. doi:10.1002/anie.201006023

Theberge AB, Courtois F, Schaerli Y, Fischlechner M, Abell C, Hollfelder F, Huck WT (2010) Microdroplets in microfluidics: an evolving platform for discoveries in chemistry and biology. Angew Chem Int Ed 49(34):5846–5868. doi:10.1002/anie.200906653

Utada AS, Lorenceau E, Link DR, Kaplan PD, Stone HA, Weitz DA (2005) Monodisperse double emulsions generated from a microcapillary device. Science 308(5721):537–541. doi:10.1126/science.1109164

van der Graaf S, Schroën CGPH, Boom RM (2005) Preparation of double emulsions by membrane emulsification—a review. J Membr Sci 251(1–2):7–15. doi:10.1016/j.memsci.2004.12.013

Villar G, Heron AJ, Bayley H (2011) Formation of droplet networks that function in aqueous environments. Nat Nanotechnol 6(12):803–808. doi:10.1038/nnano.2011.183

Wang W, Xie R, Ju X-J, Luo T, Liu L, Weitz DA, Chu L-Y (2011) Controllable microfluidic production of multicomponent multiple emulsions. Lab Chip 11(9):1587–1592. doi:10.1039/C1LC20065H