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PAPER

Single step emulsification for the generation of multi-component double emulsions

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We successfully encapsulate two, three, and four different inner drops inside double emulsions by means of a single-step emulsification technique. The microfluidic device fabrication is simple and the emulsification process highly robust. Optical microscopy images of double emulsion generation and of monodisperse double emulsions with discrete numbers of inner drops indicate the achievement of a high level of control with this technique. When the middle fluid transitions from dripping to jetting, two additional variations of double emulsions are produced: highly packed double emulsions and double emulsions with different sizes of inner drops. Finally, we successfully coalesce inner drops confined in a wax shell by applying heat. This demonstrates that these multi-component double emulsions may be useful as micro-reactors.

I. Introduction

Double emulsions, smaller droplets of one fluid suspended in a larger droplet of a second, immiscible fluid, are important for technologies utilizing encapsulation and release of active ingredients.[1–7] Generating large quantities of double emulsions is possible with bulk techniques where two sequential emulsification steps are used: the first step involves mixing the innermost dispersed phase in a second fluid, which then becomes the dispersed phase in the next emulsification step. Since individual droplet formation is not regulated, the size and number of inner droplets and the size of outer droplets are poorly controlled.[8,9] In contrast, an alternative emulsification technique using microfluidic devices offers exquisite control over the number and size of encapsulated droplets by regulating the production of individual droplets.[10–12] The precise control over droplet size and number and the high efficiency of their encapsulation makes these structures ideally suitable for actives such as drugs, nutrients, cosmetics and reactants; they can be loaded within the innermost drops and the double emulsion structure will offer suitable encapsulation.

However, it remains challenging to controllably encapsulate more than one type of active in drops and pack drops with a high density of multiple components: the difficulty lies in controllably loading several distinct drops inside larger drops while still maintaining their number ratio and stability. Yet, to advance potentially important applications, it would be valuable to encapsulate different types of drops for later release of incompatible actives or for using multi-component drops as isolated microreactors loaded with different reagents. For example, as discrete microreactors, the inner drops can be triggered to coalesce and react with each other; this can be accomplished with heat if the outer drop is composed of a thermo-responsive material such as wax and heated to a temperature close to its melting point.

Recently reported was a microfluidic approach describing the generation of double emulsions with two and three different species of inner drops. These multiple component double emulsions are produced with separate glass capillaries for each inner phase and they use a two-step sequential emulsification procedure, similar in concept to bulk techniques. The continuous carrier fluid in the first step becomes the dispersed fluid in the next step: inner drops are generated upstream, while the encapsulation of these inner drops occurs downstream in the device.[13,14] However, this two-step emulsification technique suffers from the requirements of synchronization of both inner and outer droplet production and intricate device fabrication. This motivates an alternative approach for easier device fabrication and operation to form multi-component double emulsions.

In this paper, we show a pragmatic and facile approach for generating double emulsions with two, three, and four different types of inner drops. We use dual,[15] triple and quadruple bore injection capillaries with distinct inner channels to separate each of the fluids which are emulsified to form individual inner drops inside double emulsions. At a single location in the device, inner and outer droplets are formed while almost simultaneously the inner drops are encapsulated inside the outer drops. We call this a single step emulsification technique.[16]

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A key feature of this technique is the design of microfluidic devices; the design has important consequences in simplifying device fabrication, device operation, and the generation of unique double emulsion configurations. The simplicity in device fabrication lies in only having to align the orifices of the multiple-bore injection capillary to the orifice of the collection capillary. This facilitates device fabrication. Device operation is also simplified as the fluid flow rates for the generation of inner and outer droplets do not have to be synchronized. For example, by adjusting the volumetric flow rates of the fluids independently, the number and size of inner drops as well as the size of outer drops are easily manipulated because the fluids are distinct from each other. That is, it is not necessary for the continuous carrier fluid to operate as the dispersed fluid as in previously mentioned work.[13,14]

While our device fabrication and its operation provide an easy route to forming multi-component double emulsions, generating double emulsions with new configurations and the ability to uniquely compartmentalize their internal space are particular advantages of our technique. These unique arrangements of inner drops within the emulsions occur almost immediately upon encapsulation with the resulting configurations dependent on the number and size of inner drops. The opportunities provided by these unique configurations are not yet foreseen; however depending on the fluids that comprise the emulsions, we envision programmable and active double emulsions based on the arrangement of inner drops.

Interior drops are stabilized either with oil containing surfactants or with a molten wax used as the middle phase; these stabilizing fluids prevent the inner drops from cross-contamination and coalescence.[17,18] Finally, we show that after production of wax stabilized double emulsions, we thermally trigger the inner drops to coalesce with each other inside their confining drop; this demonstrates that these isolated microreactors can be used for chemical reactions inside drops provided real reagents that are immiscible with oil are used.

II. Materials and methods

A. Materials

To prepare emulsions, we use the following fluid compositions: the outer phase contains water (18.2 MΩ cm^{-1}, Millipore Milli-Q system) with 10% poly(vinyl alcohol) (PVA; M_w: 13 000–23 000 g mol^{-1}, 87–89% hydrolyzed, Sigma-Aldrich Co.), the middle phase contains either kerosene with 8% PGPR-90 and 2% Abil-EM-90 or Suppocire AIM oil (mixture of triglycerides of saturated fatty acids from C8–C18, melting point range between 27–44 °C, Gattefosse), and the inner phase contains water (18.2 MΩ cm^{-1}, Millipore Milli-Q system) with either Allura Red (Sigma-Aldrich), green food coloring (McCormick), Toluidine Blue (Spectrum) or Wright Stain Blue (Sigma-Aldrich) dyes.

B. Preparation of devices

Capillary microfluidic devices are fabricated with dual, triple, and quadruple bore and square glass capillaries purchased from Atlantic International Technology (AIT) while the collection glass capillaries are purchased from World Precision Instruments and have an inner diameter of 0.84 mm and an outer diameter of 1.5 mm. The dual bore glass capillary has an outer diameter of 1.55–1.65 mm, a bore size of 400 microns, and a septum of 0.635 mm. After tapering, the orifice of each bore has a diameter of 10–20 μm, with a septum of 25 μm. The square capillary that both the multi-bore injection and collection capillaries fit into has an ID of 1.75 mm. The capillaries are tapered using a micropipette puller (Sutter Instrument Co, Model P-97).

Before inserting the capillaries into the square capillary, the tip of the multi-bore capillary is dipped into a solution of trimethoxy(octadecyl)silane (Sigma-Aldrich) to make its surface hydrophobic while the orifice of the collection capillary is treated with 2-[methloxy(polyethyleneoxyl-propyl]9-12 trimethoxysilane (Gelest) to make its surface hydrophilic. With these silane coatings, the fluids move along the walls of the capillaries as shown in the schematic of Fig. 1a.

C. Device operation

We use glass syringes and the syringes with Harvard PHD 2000 series syringe pumps. Teflon tubing (Scientific Commonities-PE5) is used to connect the syringes to the microfluidic devices. Typical flow rates for generating multi-component double emulsions are – outer: 10 000–20 000 μL h^{-1}, middle: 2000–3500 μL h^{-1}, and inner, each: 100–1000 μL h^{-1}.

D. Sample characterization

Monitoring double emulsions as they are generated is possible by viewing the capillary device using an inverted optical microscope (DM-IRB, Leica) fitted with a fast camera (Phantom 9, Vision Research). After fabrication, the emulsions are imaged on a glass slide with a Nikon Inverted microscope (TE2000-E) equipped with a Nikon Color digital camera (Sight DS-U1). Temperature responsive measurements are also recorded with a fast camera fitted to an inverted optical microscope. Heat is applied to the wax emulsions with a heat gun and the temperature is measured with a thermocouple probe that is connected to a handheld thermometer.

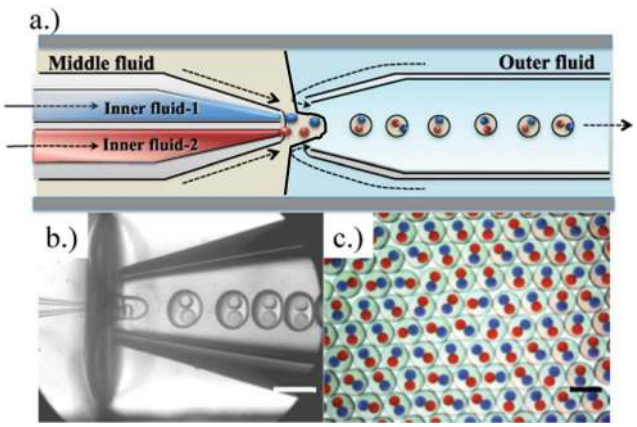

Fig. 1 (a) Schematic of a microfluidic capillary device for preparation of multiple component double emulsions using a single-step emulsification. (b and c) Optical microscopy images showing double emulsion generation and monodisperse double emulsions with two different inner drops, one red and one blue, produced at Q_{red} = 300 μL h^{-1}, Q_{blue} = 400 μL h^{-1}, Q_{middle} = 2000 μL h^{-1}, and Q_{outer} = 15 000 μL h^{-1}. The scale bars represent 100 μm.

III. Results and discussion

A. Generating double emulsions with two different types of inner drops

To produce monodisperse double emulsions with two different types of inner drops, we use glass capillary microfluidics with a cylindrical tapered injection tube containing two bores and a cylindrical tapered collection tube containing a single bore. These are inserted inside a square capillary as shown in the schematic of Fig. 1a. The orifices of the cylindrical capillaries are co-axially aligned with each other and sealed in place with an epoxy resin.[10] The custom designed dual bore glass capillaries are engineered so that, after tapering, the bores are spaced sufficiently far apart to prevent the emerging drops from coalescing with each other before undergoing encapsulation.

During droplet generation, and in particular, with this single step emulsification technique, several processes occur simultaneously: distinct drops of two different types are generated at the orifices of the injection capillary while the middle phase emulsifies the emerging drops. The continuous phase focuses the middle phase into drops or a jet that subsequently breaks up to form double emulsions with distinct inner drops. These double emulsions are formed in the spatially confined collection tube near its opening as seen in the optical microscopy image in Fig. 1b. We inject two different aqueous solutions containing either toluidine blue or Allura Red dye into each of the dual bore channels; the middle fluid is injected into the interstices of the square and the injection capillaries and consists of oil with surfactants. The aqueous continuous fluid is injected into the interstices of the square and collection capillaries.

When inner, middle and continuous fluids converge to the same location in the device by both co-flow and flow focusing hydrodynamics, two distinct regimes of flow patterns form inside the collection tube based on the flow rates of the inner and middle fluids: dripping or jetting.[19] Because the spacing between the bores in the injection capillary is significant, the two inner fluid streams emerge as two separate streams from the capillary; eventually, by modulating the fluid flow rates, distinct inner drops form due to pinchoff from their respective orifices with one drop leaving its orifice slightly ahead of the other drop. At low flow rates for all fluids, and therefore in the dripping regime for both inner and middle fluids, the number of aqueous inner drops is limited to small numbers as shown in Fig. 1. Increasing the flow rate of the middle fluid into the jetting regime results in the encapsulation of large numbers of inner drops when the inner drops are generated in the dripping mode; when the inner drops are generated in the jetting mode, inner drops that are large in size are encapsulated. Depending on in which regime the device is operating, dripping or jetting, for the middle and inner fluids, three variations of double emulsions can be produced.

B. Dripping regime of the middle fluid

In the dripping regime, we controllably load precise numbers of two different types of inner aqueous drops inside oil drops for the generation of monodisperse water–oil–water double emulsions. The number of inner drops is expressed as the ratio of the frequency of generation of inner drops to the frequency of generation of outer drops. This ratio can be written in terms of the flow rates of the red and blue inner fluids, Q_{red} and Q_{blue}, and the flow rate of the middle fluid, Q_{middle} with the volume of the drops given by mass conservation of the fluid streams.

For example, the number of red aqueous drops, N_{red}, encapsulated in a single outer drop can be expressed as:

$$N_{red} = \frac{f_{red}}{f_{outer}} = \frac{Q_{red}}{V_{red}} \times \frac{V_{outer}}{Q_{red} + Q_{blue} + Q_{middle}}$$

where $V_{red} = \frac{4}{3}\pi R_{red}^3$ and $V_{outer} = \frac{4}{3}\pi R_{outer}^3$ with the radii of the red and outer drop given as R_{red}, and R_{outer}, respectively. We can precisely control the number of red and blue inner drops that are encapsulated as shown in Fig. 2. The experiments for the generation of double emulsions with two different inner drops using a single microfluidic device are summarized in the plot of control parameters Q_{red} against Q_{blue} in Fig. 3.

From the above equation it follows that $N_{red}/N_{blue} = f_{red}/f_{blue} = Q_{red}/V_{red} \times V_{blue}/Q_{blue}$. Therefore, double emulsions containing monodisperse inner drops ($V_{red} = V_{blue}$) with equal numbers of red and blue drops are produced using identical flow rates $Q_{red} = Q_{blue}$. These fall close to or on the bisectional line in the plot of Fig. 3. Slight differences between the volume of the red drop, V_{red}, and the volume of the blue drop, V_{blue}, as in the case of 1r, 1b and 2r, 2b are the reasons for the deviation from the bisecting line in Fig. 3. For example, encapsulating one red and one blue drop with flow rates: $Q_{red} = 300\ \mu L\ h^{-1}$ and $Q_{blue} = 400\ \mu L\ h^{-1}$, results in the radius of the blue drop being slightly larger than the radius of the red drop, $R_{blue} \sim 1.1\ R_{red}$ as shown in Fig. 1b and c.

The bisecting line divides the graph into two regions: $N_{red}/N_{blue} > 1$ or $N_{red}/N_{blue} < 1$. For example, with $Q_{blue} = 500\ \mu L\ h^{-1}$, as Q_{red} is changed to 300–900 $\mu L\ h^{-1}$, N_{red}/N_{blue} goes from 0.5 to 1.5. This "phase" diagram indicates desired numbers of each inner drop are encapsulated through independent control of Q_{red} and Q_{blue}.

A table of possible configurations of two different inner drops inside another drop is given in Fig. 4. This tabulation displays the range of configurations that are possible when operating the

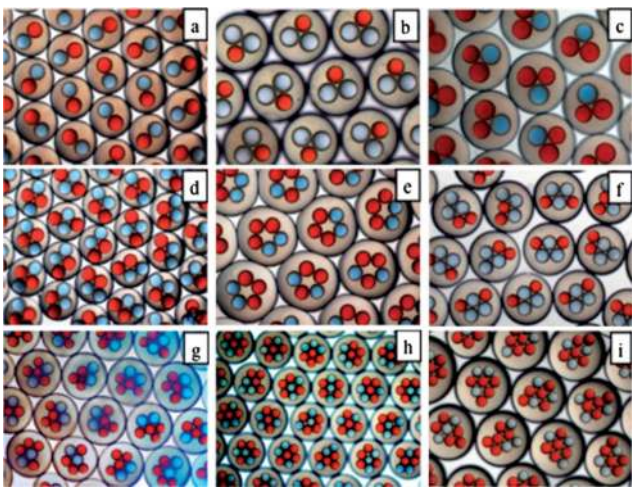

Fig. 2 Combinations of monodispersed double emulsions with two different types of inner drops for configurations of: (a) two, (b and c) three, (d) four, (e and f) five, (g) six, (h) seven, and (i) eight total inner drops. These double emulsions are produced from several different devices.

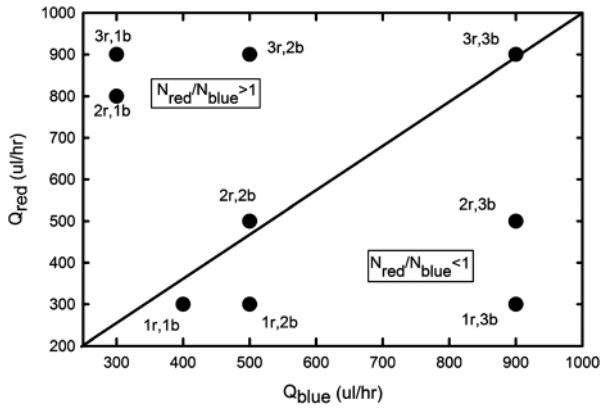

Fig. 3 A plot of inner flow rate for red drops, Q_{red} *vs.* the inner flow rate for blue drops, Q_{blue} for double emulsions with two different inner drops. The labels on the data points refer to the number of drops colored either red, r, or blue, b. The data are taken from double emulsions produced from a single device.

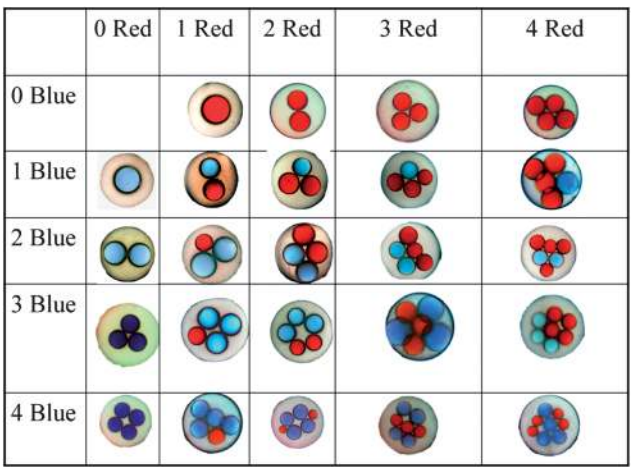

Fig. 4 A table of different combinations of double emulsions with two different types of inner drops.

device in the dripping regime with this single step emulsification technique. This table is a compilation of double emulsions from more than one device.

C. Jetting regime of the middle fluid

With increasing flow rate of the middle phase, a transition from dripping to jetting of the outer drop is observed. Depending on the regime of inner drop generation, we can produce two different types of double emulsion drops. When inner fluids are dripping, and the middle fluid is jetting, large numbers of inner drops are encapsulated in the outer drop, as shown in Fig. 5a. The frequency of inner drop generation is higher than that of breakup of the widening jet of the middle phase, so that the number of inner drops can be very high as shown in Fig. 5b and c. For example, similar numbers of red and blue drops are encapsulated when we operate the device with $Q_{red} = 1000$ μL h^{-1} and $Q_{blue} = 1000$ μL h^{-1}, as shown in Fig. 5b. When we operate the device with $Q_{red} = 400$ μL h^{-1}, and $Q_{blue} = 1000$ μL h^{-1}, four times more blue drops are encapsulated than red drops as shown in Fig. 5c.

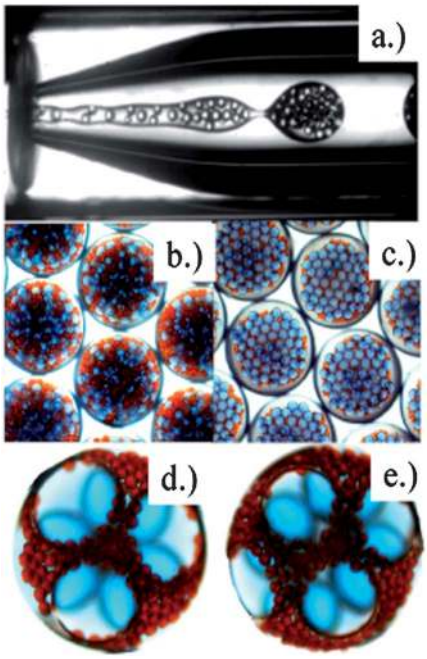

Fig. 5 (a) Optical microscopy image showing double emulsion generation with the middle fluid in the jetting regime and the two inner fluids in the dripping regime. (b and c) High density double emulsions with two different inner drops. (d and e) Stable and unique double emulsion configurations of inner drops with two different sizes: large blue drops, 170 μm in diameter combined with much smaller red drops, 30 μm in diameter.

By employing both dripping and jetting modes of inner drop generation in two bores of the injection capillary, we can encapsulate two different sizes of inner drops into outer drops. When we increase the flow rate of one of two inner phases, the inner phase flows in a form of a jet; this jet breaks into large drops prior to breakup of the middle jet. Therefore, we encapsulate large inner drops as well as small inner drops made in the dripping regime. Simultaneously the frequency of breakup of the inner jet is controlled by the flow rate of the inner phase, enabling control of the number of large inner drops as well. For $Q_{blue} = 2000$ μL h^{-1} and $Q_{red} = 200$ μL h^{-1}, resultant double emulsions have six large blue drops of 170 μm and tens of small red drops of 30 μm, as shown in Fig. 5d, where six large drops are arranged in a unique configuration, an octahedron, to minimize interfacial energy, while the small drops fill the interstices between the large drops. Another example, composed of eight large drops, is shown in Fig. 5e.

D. Generating double emulsions with three and four different types of inner drops

To make these double emulsions even more versatile, we encapsulate three different types of drops by using a triple bore capillary where the three bores are in a triangular arrangement to keep the distance as far apart as possible. In a similar fashion to dual bore capillaries, we operate the device with two different regimes of outer drop breakup, resulting in three different types of double emulsions with three different components. For example, by operating the device in dripping regime for both

breakups of the inner and middle fluids, we produce double emulsions with small numbers of three different inner drops as shown in Fig. 6a, where two blue, one red and two transparent inner drops are encapsulated on average. Additionally by operating in the dripping regime for inner drop generation and jetting regime of outer drop generation, we can encapsulate tens of three different types of inner drops in the outer drops as shown in Fig. 6b. For operating in dripping of blue and red inner drop generation and jetting of transparent drop generation, we obtain one large transparent inner drop with blue and red inner drops filling the interstices between the large drop and the perimeter of the outer drop with additional coverage on top of the large inner drop as shown in Fig. 6c. Similar configurations of double emulsions are shown in Fig. 6d except in this case the red and blue drops merged at the orifice of the injection capillary to form purple drops. Optical microscopy images of the generation and the resulting monodisperse double emulsions for the case with small red and blue drops and one large transparent inner drop, Fig. 7a and b, and two large transparent inner drops that form dimers are shown in Fig. 7c and d.

Additional expansion of the number of components is achieved by using multi-bore capillaries as injection capillaries; we encapsulate four different inner drops using quadruple bore capillary as shown in Fig. 8. Like the case with dual bore capillary devices, high inner flow rates enable large numbers of inner drops to be captured inside the outer drop; the surfactant in the middle phase prevents the inner droplets from coalescing with one another.

E. Triggered coalescence of inner drops

To perform chemical reactions inside double emulsions and independent of the microfluidic device, it is necessary to trigger coalescence of the inner droplets containing different reactants. To prepare capsules with inner drops that can be triggered outside of the device, we use a temperature responsive wax as the middle phase. This approach has the distinct advantage of

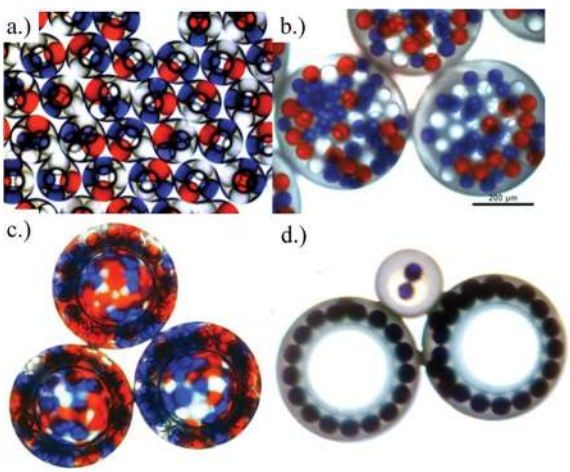

Fig. 6 Optical microscopy images of double emulsions generated using a triple bore injection capillary. Double emulsions with three different inner drops: red, transparent, and blue for (a) small numbers of inner drops, (b) high density of small inner drops and different sizes of inner drops with (c and d) one large transparent inner drop. For (d) the red and blue drops merged to form purple drops.

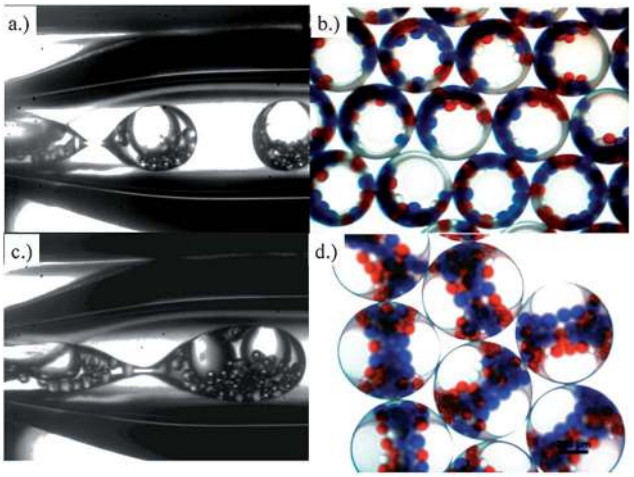

Fig. 7 Optical microscopy images showing double emulsion generation and monodisperse double emulsions with three different inner drops, red, transparent, and blue. The double emulsions have several red and blue drops of the same size and (a,b) one large transparent inner drop and (c,d) two large transparent inner drops that form dimers.

stabilizing inner drops without the use of surfactants that hinder triggered coalescence. Double emulsions with a waxy shell are prepared in capillary devices where the entire device and wax filled syringe are heated to keep the wax molten; these emulsions are then collected in water at a temperature where the middle phase solidifies. The resultant dispersion is stored in room temperature water without degradation or evaporation of the reagents for long periods of time, up to fifteen months. Applying sufficient pressure to crack or break the wax stabilized emulsions is possible by placing the emulsions between two glass slides as shown in Fig. 9; the significant pressure needed to break or crack the emulsions confirms their mechanical stability.

A simple trigger mechanism, heat from a hot air gun, is used to melt the outer shell and activate coalescence of the low viscosity inner drops. Coalescence occurs when the inner drops are close enough together that a bridge develops between them. As the temperature increases to the melting point of the wax, 27–44 °C, inner drops begin to mix due to convection and coalesce upon droplet collision. Eventually all inner drops coalesce with one another until finally only one drop remains. The case for six aqueous inner drops converging one by one to a single inner drop is shown in Fig. 10. This technique demonstrates that chemical

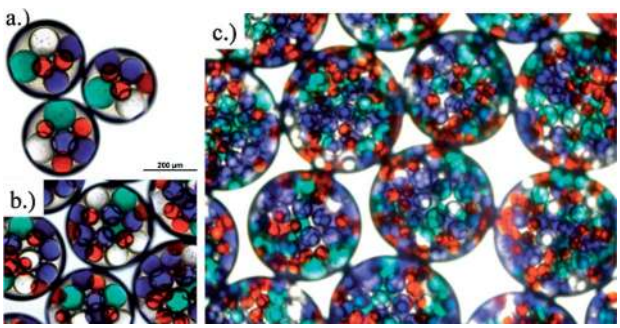

Fig. 8 Double emulsions with four different types of inner drops: red, transparent, blue, and green: (a and b) small numbers of inner drops and (c) high density of inner drops.

Fig. 9 Wax-stabilized double emulsion (a) before applying pressure between two glass slides and (b and c) with increasing pressure from b to c to break the double emulsion. The scale bar represents 400 μm.

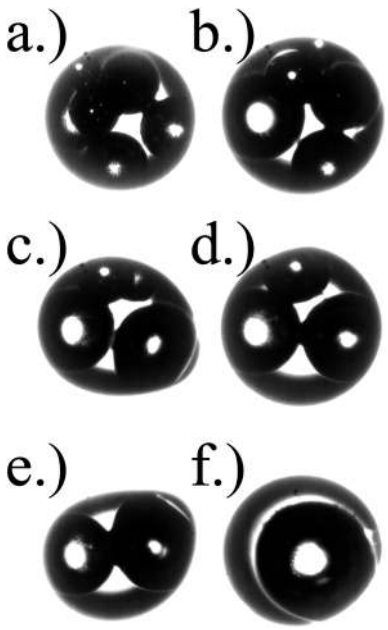

Fig. 10 Coalescence of inner aqueous drops confined inside a wax drop. As the temperature increases, the wax melts and the inner drops move closer together and coalesce. In the time lapse series shown, the number of inner drops decrease from: (a) 6 drops to (b) 5 drops to (c) 4 drops to (d) 3 drops to (e) 2 drops to (f) 1 drop.

reactions inside emulsions that are outside of the device may be possible as long as the reagents used are immiscible with the molten wax.

IV. Conclusions

Exquisite control over the number, size, and type of inner droplets inside double emulsions is possible using dual, triple, and quadruple bore glass capillary devices. Implementing a multiple bore capillary into a typical glass microfluidic device is simple and leads to robust fabrication of double emulsions with either discrete or large numbers of inner droplets and multiple compartments within the double emulsions. Moreover, they demonstrate that large numbers of encapsulated drops with tunable sizes can be stabilized inside another drop. We also demonstrate the generation of thermo-responsive emulsions using molten oil as the middle phase that may be useful as microreactors for chemical reactions inside drops and outside of devices in the foreseeable future. These microreactors could also provide a platform for combinatorial chemistry of valuable or scarce reagents at lower cost than conventional analysis while permitting thousands of individual reactions to be analyzed.[20]

Acknowledgements

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