Tailored Double Emulsions Made Simple

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Double emulsions, such as water-in-oil-in-water droplets, are important material platforms for conducting fundamental research and for technological applications. To date, well-defined double-emulsion droplets consisting of a single water core and a thin oil shell can be exclusively formed with sophisticated microfluidic devices. The fabrication, preparation, and operation of such devices is challenging, which reduces the availability of tailored double emulsions to a limited community of experts. Here, a simple method is introduced to produce single-core double emulsions with high yield in large quantities, using a vortex mixer. Utilizing the density difference between the dispersed droplet and the continuous phase, this two-step emulsification method can achieve very small core droplet diameters below 10 μm and ultrathin shells with thicknesses below 1 μm. A detailed picture of the formation mechanism is provided and it is demonstrated that the process can be extended to produce multishell and multicore emulsions. Finally, its application is demonstrated to produce structurally colored colloidal supraparticles with unprecedented uniformity and yield. The method allows the creation of tailored double emulsions with minimal time, cost, effort, and expertise, and may widen its application to nonspecialized scientific communities.

1. Introduction

Double emulsions are droplets inside droplets. Most commonly formulated as water-in-oil-in-water (w/o/w) droplets, such emulsions serve as an important material platform for picoliter-sized liquid encapsulation and compartmentalization. They can be produced at high throughputs by two-step emulsification processes, where water is first emulsified in oil by high-energy homogenization, before the first emulsion is re-emulsified in a second aqueous phase.[3] Unfortunately, the resulting droplets lack structural uniformity—multiple water droplets are often encapsulated in one oil droplet and their size distribution is wide. Single-core double emulsions (SCDEs), consisting of only one water droplet in one oil droplet, provide a well-defined droplet structure and hence controlled material transport between the dispersed and continuous phase. Therefore, they are ideal model systems that are especially beneficial for biological, biomedical, and chemical screening assays. For example, they are used to encapsulate biological entities for miniature cell culture,[2–4] high-throughput biological or chemical screening assays,[5,6] and as model systems for the understanding of self-assembly and phase behavior in soft matter.[7–12] In addition, they template the fabrication of microparticles[13] and polymer capsules[14,15] for drug delivery and release, as well as colloidosomes,[16] polymersomes,[17] and liposomes.[18–20]

Microfluidics has been the gold standard to produce double emulsions containing only a single core per drop and possessing well-defined dimensions.[14,19,21–28] However, the fabrication of microfluidic devices that produce such calibrated double emulsions, particularly those whose shell does not occupy a considerable percentage of the double-emulsion volume, is challenging (Figure 1a). To reduce the volume occupied by the shell and thereby increase the loading capacity of the double emulsions, special glass capillary devices have been introduced. These devices produce SCDE with ultrathin shell of a few hundred nanometers.[21,29] However, the droplet diameters are comparably large, around 100 to 200 μm, limited by the opening of the hand-drawn glass-capillaries and their manual alignment.[13,16,19] In addition, the throughput is low and the reproducibility in the hand-drawn device fabrication cannot be guaranteed. The reproducibility of the device fabrication is much higher if they are made through soft photolithography. Indeed, this technology is often used to produce poly(dimethylsiloxane) (PDMS)-based microfluidic devices with well-defined channel structures. These devices enable the production of double emulsions with shells whose thickness is below 1 μm.[23,30,31] Nonetheless, successful device fabrication requires complex, 3D channel architectures, precise alignment of different channel parts, and challenging surface treatments of the different channel segments only a few dozen micrometers apart.[32–34] In addition, the serial nature of microfluidics limits throughput and scalability. The throughput can be increased if devices are parallelized. Indeed, SCDE can be produced at rates up to 10 mL h−1.[25] Much higher throughputs up to 1000 mL h−1 can be achieved for single emulsions.[35,36]
Methods that enable the controlled production of double emulsions at low cost and high rates remain to be established. Here, we introduce a method to produce double emulsions with single cores and micrometer-thin shells using a conventional, lab-scale vortex mixer. This process exploits the density difference between the droplet and the continuous phase for the double emulsification and readily produces well-defined w/o/w or o/w/o droplets at milliliter per minute rates. The method allows emulsification of a wide range of fluids, is scalable, and compatible with microfluidic devices if monodisperse droplets are desired.

2. Results and Discussion

2.1. Two-Step Double Emulsification

As a model oil, we employ a perfluorinated oil (HFE 7500) that is commonly used in microfluidic devices to produce emulsions (Figure 1b). The desired dispersed water phase is pipetted into the oil phase in a centrifuge tube. To avoid droplet coalescence, we add 1 wt% commercial fluorosurfactant Krytox (FSH 157) to the oil. The liquid mixture is vortexed to create a single w/o emulsion. We prepare a second aqueous phase that contains 1 wt% sodium dodecyl sulfate (SDS) to stabilize the final double-emulsion droplets. The w/o emulsion (appearing white in Figure 1c) is pipetted into this second aqueous phase that is contained in a second centrifuge tube. When the w/o emulsion is pipetted into the continuous water phase, it spontaneously forms an ill-defined w/o/w double emulsion with large numbers of water cores per oil droplet at the bottom of the container. These large droplets break up into w/o/w SCDE when vortexed (detailed protocol in Figure S1 in the Supporting Information). The resulting SCDE has an average diameter of 40 µm and an oil shell thickness of a few micrometers (Figure 1d; Figures S2–S4, Supporting Information). Importantly, despite the simplicity of the process, the yield of single-core droplets is very high (>99%). The method produces milliliters of SCDE per batch in minutes and can be scaled using larger containers and stronger vortex shearing. The resulting SCDE are stable for at least six months. More generally, the stability of the double emulsion depends on the formulation, rather than the emulsification process, and should be very similar to the those produced with complex microfluidic devices.[37,38]

This simple emulsification method features two surprising properties. First, it yields nearly complete SCDEs. Second, the oil shell surrounding the droplets is uniform in thickness. These properties distinguish the process from other non-microfluidic emulsification techniques, which can only produce multiple water cores and thick, nonuniform oil shells.[9] To better...
understand, visualize, and characterize the formation mechanism, we use monodisperse w/o droplets produced in a conventional droplet-based microfluidic device as a feed (Figure S5, Supporting Information), as previously reported by Sukovich et al. The w/o/w double emulsion initially contains a large number of water core droplets, as exemplified in Figure 2a-i–iv. Vortexing the container continuously discretizes the large oil droplets, until each droplet only contains a single water core, with a uniform size inherited by the feed emulsion. We note that the SCDE using such a feed emulsion has less small accompanying empty single-emulsion droplets than those produced solely by vortexing, as the monodisperse cores pack more efficiently and therefore reduce the total amount of oil in the formed double emulsion, as detailed below (Figures 1d and 2a; Figure S6, Supporting Information).

2.2. Yield of Single-Core Double Emulsions

Using monodisperse emulsions as model systems, we explore the influence of process parameters on the yield of SCDE (Figure S7, Supporting Information). The yield of SCDE increases with increasing core droplet size, under the specific tested conditions (2500 rpm vortex, 15 mL centrifugation tubes, and 1 mL water as continuous phase with 1.0 wt% SDS surfactant; details in the Supporting Information), as shown in Figure 2c-i. Interestingly, for all core sizes, the yield rapidly increases upon vortexing and plateaus after 15 s (Figure S8, Supporting Information). The yield of SCDE is strongly influenced by the total liquid volume: reducing the volume of the continuous water phase from 3 to 0.2 mL significantly increases the yield from 20% to 90% (for droplets with core diameters of 30 µm; Figure 2c-ii, blue; Figure S9, Supporting Information). We attribute this increase to the reduced thickness of the water film formed at the centrifuge tube wall during vortexing, estimated via the rise of water level (Figure 2c-iii, green; Figure S10, Supporting Information). Similarly, the yield of SCDE is strongly influenced by the centrifugal forces generated in the vortexing step. Higher centrifugal forces substantially increase the yield (Figure S11, Supporting Information), which can be achieved by either increasing the vortex speed or the diameter of the centrifuge tube (Figure 2c-iv; 15 mL tube has a diameter of 2 cm, 50 mL tube of 4 cm). If these parameters are optimized, we obtain a near-quantitative conversion of the feed w/o emulsions into w/o/w SCDE with core sizes between 30 to 100 µm (Figure 2b,f; Figure S7, Supporting Information). Note that the surfactant concentration barely influences the yield, provided that the concentration is sufficient to prevent recoalescence of the formed SCDE (for SDS, around 0.1 wt%), underlining the robustness of this method (Figure 2c-ii; Figure S12, Supporting Information). Such robustness and quantitative yield may enable its integration with advanced single-emulsion-producing devices for high-throughput uniform SCDE formation.

From our observations, we deduce a physical picture of the emulsification process underlying this method (Figure 2d). Key to a successful breakup of the multicore w/o droplets is the formation of a thin liquid film of the continuous phase during vortexing. The rotating liquid generates a shear force parallel to the wall, whose magnitude is controlled by the film thickness (i.e., the total liquid volume; see Figure 2c-iii), the rotational speed (Figure 2c-iv) and the viscosity of the continuous phase. Importantly, w/o droplets have a higher density than the continuous water phase as they contain perfluorinated oil (1.6 g cm⁻³). As a result, centrifugal forces generated during vortexing push the droplets toward the container wall, exerting friction to resist the droplets' lateral motion at the wall (Figure 2c-iv). Together, the shear force and the friction collaborate to break up the multicore oil droplets into single-core double-emulsion droplets (Figure 2e). This mechanism also defines the boundaries of the droplet sizes. For smaller droplets, the required shear force and friction becomes higher, until a critical point when the centrifugal force is too strong such that the core droplets deform and break. There is no intrinsic upper size boundary for larger droplets, as they require lower shear and friction, which can be achieved via slower vortexing speeds. The exact size boundary depends on the experimental parameters, such as vortexing speed, centrifuge tube diameter, volume of continuous phase, and so on, as we have demonstrated above. Note that this process not only discretizes the multicore droplets into single-core droplets, but also reduces the shell volume to form thin shells (Figure 2e-viii). The excess oil that is sheared off typically remains in the system in the form of small oil-in-water single-emulsion droplets that coexist with the SCDE (Figure 2b,e; Figures S15–S17, Supporting Information). If needed, the small oil droplets, having a different density and typically very small sizes, can be separated in an additional processing step.

2.3. Shell Thickness of Single-Core Double Emulsions

Many properties of double emulsions, such as their permeability and stability, depend on the thickness of their shell. An interesting observation is that SCDE produced in our method have a constant oil shell thickness at about 3 µm, independent of the core diameter or polydispersity. To test if we can tune the shell thickness of SCDE produced with our method, we vary the friction between droplets and the container wall. We expect that during the lateral movement of droplets at the container wall, friction effectively removes excess oil in the shell. As the volume of the oil shell decreases, the density difference between the SCDE and the continuous phase also becomes smaller, resulting in lower friction. This self-limiting process suggests a critical oil shell thickness that can be tuned by varying the density of the involved phases. We test this hypothesis by adding between 0 and 50 vol% ethanol to the continuous to reduce the density of the continuous phase and thus increase the density difference by up to +0.07 g cm⁻³. Recall that the emulsion droplets are heavier due to the perfluorinated oil shell. Indeed, with higher density difference, the double-emulsion shell thickness decreases from 3 to 1 µm (Figure 3a,b; Figure S13, Supporting Information). However, adding ethanol also alters the viscosity and the interfacial tension of the continuous phase, which may influence the shell thickness. To elucidate which of these properties governs the change in shell thickness, we increase the density of the water core droplet by using deuterated water, which also result in a +0.07 g cm⁻³ density difference without affecting viscosity of the continuous phase or interfacial tension. The resulting shell thicknesses are...
Figure 2. Mechanism of the simple single-core double-emulsion production. a) Microscopy images showing the break-up of multicore w/o/w double emulsions into increasingly smaller droplets during vortexing, until eventually only single-core droplets remain. b) Monodisperse w/o/w double emulsions can be obtained using w/o emulsions produced in standard PDMS microfluidics as a feed. Uniform single-core double emulsions with diameters ranging from 30 to 100 µm can be produced with high yield in our simplistic setup. c) Influence of process parameters on the yield of single-core double emulsions: i) the yield plateaus after short vortexing time and decreases with decreasing water droplet sizes; ii) the surfactant concentration does not increase the yield once the concentration is sufficient to prevent recoalescence of the formed single-core double emulsions; iii) the yield increases with decreasing volume of the continuous water phase (blue data), which reduces the water film thickness during the vortexing step (green data); iv) the yield increases with increasing centrifugal forces, implemented by using higher vortexing speeds or a centrifuge tube with a larger diameter. d) Forces in the single-core double-emulsion formation mechanism: during vortexing, shear forces in the water film break up the multicore droplets until each oil droplet contains only a single water core. The process is facilitated by centrifugal force that pushes the droplet toward the centrifuge tube wall, where friction regulates the thickness of the oil shell. e) Schematic illustration of the droplet break-up mechanism. i) The interface of multicore droplets in contact with the wall deforms around the water cores, ii,iii) to form smaller oil droplets, iv) containing lower numbers of water cores. v,vii) The process continues to increase the yield of single-core droplets. vi) The process simultaneously creates small oil-in-water single-emulsion droplets from removal of excess oil by droplet break-up and partial removal of the shell. The oil-removal process is self-limiting, as it decreases the droplet density, which reduces the centrifugal force and friction acting on the droplets. viii) As a result, the shell thickness converges and does not decrease further. f) Representative microscopy image of single-core double emulsions with 30 µm diameter water cores, underlining the high yield and low polydispersity in core and shell thickness.
very similar to those obtained for systems containing ethanol, suggesting that the density difference between the droplet and the continuous phase is the dominant parameter controlling the shell thickness (Figure S14, Supporting Information). Hence, the uniform shell thickness is an inherent result by our emulsification method, regardless of the core droplet size (Figure 2) and even in the case of polydisperse core droplets (Figure 1). In fact, friction has been utilized in some sophisticated microfluidic devices to reduce double-emulsion shell thickness, i.e., by squeezing droplets through narrow channels or porous membranes.\cite{22,41} Our method is conceptually similar, yet experimentally simpler.

We notice that the SCDE produced with 50% ethanol–water mixtures start to lose their uniformity and form smaller droplets. This suggests that the large density difference increases the centrifugal force such that the core droplets deform and break. This process might be facilitated by the reduction in the interfacial tension that is caused by the addition of ethanol. Noteworthily, despite these ruptures, the resulting double emulsions retain their single-core character. We utilize this feature to produce unprecedentedly small double emulsions. Using a 60 vol% ethanol/water mixture as the continuous phase, we increase the efficiency of core break-up and produce SCDE with an average diameter of 6 \( \mu \)m and an ultrathin shell with thickness below 1 \( \mu \)m (Figure 3c). The shell thickness is too thin to be accurately measured by optical microscopy. However, in transmission microscopy, thin oil shells (thickness above 1 \( \mu \)m) appear as dark rings (arrow, Figure 3c) due to the different refractive index between the oil and water. In contrast, the interface of droplets with ultrathin shells is hardly visible, suggesting reduced scattering and thus a very small thickness below 1 \( \mu \)m (Figure S15, Supporting Information).

To test the versatility of our approach, we vary the surfactant. We replace anionic Krytox surfactant contained in the oil by the nonionic, biocompatible PEG-PFPE surfactant.\cite{42} In addition, the anionic SDS surfactant contained in the aqueous phase can also be replaced by cationic CTAB, nonionic Triton, Pluronic, or PVA surfactants. We do not observe any significant change of the SCDEs when stabilized with these different surfactants. The approach can also be applied to produce o/w/o double emulsion using lighter alkane oil such as mineral oil (Figure S16, Supporting Information). Here, the continuous oil phase contains 1 wt% Span 80 surfactant and the water phase contains 1 wt% Pluronic F108. These double emulsions also have a high single-core yield (>99%) and show size dispersity without the use of microfluidics. Note that the increased amount of single-emulsion droplets relative to those observed for w/o/w SCDE described above results from the thicker water shells of multicore double emulsions. This is caused by the smaller density difference between mineral oil and water compared to water and fluorinated oil used above, and the inefficient packing of the polydisperse oil droplets in the initial o/w emulsion (Figure S6, Supporting Information). The water shell is partially removed during the shearing process, resulting in single-emulsion o/w droplets as side product. We note that although our experiments demonstrate the emulsification mechanism and practical measures to produce SCDE with a wide size range, a complete theoretical description and prediction requires further investigations.

### 2.4. Complex Emulsions

The method can be extended to create structured emulsions with increasing complexity.\cite{43–46} By repeating the procedure described in Figure 1b twice, defined w/o/w/o/w quadruple emulsions can be produced (Figure 4a). The quadruple droplets are characterized by two thin oil shells and a thick water shell. The overall yield of single-core quadruple emulsions with symmetric shell structure is about 60% (Figure S17, Supporting Information). From the optical images, we find that while small satellite droplets are sometimes found in the thicker water

\begin{figure}
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\caption{Control of shell thickness in single-core double emulsions. a) Reducing the density of the continuous phase by addition of ethanol reduces the oil shell thickness down to \( \approx 1 \) \( \mu \)m. b) Representative optical microscopy image of single-core double emulsions with decreasing shell thickness, produced with 10%, 30%, and 50% ethanol in the continuous water phase. c) A small double emulsion with an average size of 6 \( \mu \)m can be produced at even larger ethanol content of 60%. The large density difference causes break-up of the water core droplets under increased centrifugal forces, creating small single-core double emulsions with an ultrathin shell with a thickness below 1 \( \mu \)m, evident by the disappearing droplet interface in the transmission optical microscopy image.}
\end{figure}
shells, the oil shells remain essentially free of impurities. When the feed emulsion droplets have higher density than the continuous phase, the friction upon vortexing shears off excess liquid in the droplet shells down to a few micrometers, which also efficiently removes satellite droplets trapped in these shells. This applies to cases when fluorinated oil droplets are dispersed in the continuous water phase (w/o/w emulsions and w/o/w/o/w emulsions). However, when water droplets (or w/o/w droplets) are used as feed and dispersed in a continuous fluorinated oil phase (w/o/w/o emulsions), the density difference is inverted. The droplets are not pushed to the wall to create friction but are merely subjected to shear from the thinning liquid film. In these cases, the water shell remains thicker and can contain satellite oil droplets. These limitations aside, it is noteworthy that our method can yield complex emulsions without necessitating any sophisticated microfluidic device architectures, or stringent requirements for the different phases. Process modifications to improve our quadruple emulsions, such as removing empty oil droplets in the w/o/w double emulsion by filtration, sedimentation, or density matching, or controlling the water shell thickness by employing inverted centrifugal forces in a set-up with two concentric walls can be readily envisioned.

Defined multicore double emulsions can also be produced by vortexing at low speeds. While conventional microfluidic devices can accurately control the number of cores within one droplet, the total number of cores is limited due to inevitable droplet break-up in the narrow microfluidic channel. Our method can produce multicore emulsions with a large number of water cores. Although the average droplet size decreases with reduced vortexing speed, the number of cores contained in one droplet inevitably follows a distribution due to the random droplet break-up. Such systems, even with distributed numbers of cores, constitute interesting model systems to study structure formation and packing phenomena in confining elements (Figure 4b). Sphere packing in spherical confinement is well-established for solid particles but less explored for deformable liquid droplets. For small number of water cores (N = 2, ..., 9), we observe that droplets-in-droplets exhibit the same known configurations as particles-in-droplets. We find a new metastable configuration for N = 10. The pentagonal antiprism structure consists of two staggered pentagons, probably induced by the flexible oil interface at the flat substrate. For N = 12, water core droplets form an ideal icosahedron in the oil droplet, deviating from the particle-in-droplet packing controlled by surface wetting. At larger numbers of liquid cores, we find several hitherto unknown packing structures, indicating that the effect of deformability becomes increasingly important for the self-organization within the confinement. For N = 17, the liquid droplets assemble into a structure with fourfold symmetry, which is predicted by simulation of hard spheres in spherical confinement, but not known in droplet or particle experiments. For N = 38, we find a new type of droplet packing that disagrees with previous predictions in spherical confinement (Figure S18, Supporting Information). By varying the objective focus at different heights of the droplet and carefully comparing it to the sphere packing model, we find that it is a small face-centered-cubic (fcc) crystallite consisting of four layers of hexagonally packed droplets in ABCA sequence, each layer with 7, 12, 12, and 7 droplets. Interestingly, this droplet packing configuration is identical to the minimum energy structure of 38 atoms interacting with Lennard Jones potential without confinement. This unusual structure is only possible when large deformation is allowed at droplet interfaces to deviate from the spherical shape. These findings show that structure formation with deformable elements may be significantly different compared to both bulk and hard confinement. To this point, the investigation of the thermodynamics and formation kinetics of such systems has been impeded by the lack of a robust experimental platform. Our tailored double emulsions may provide a convenient way toward such experimental, all-liquid systems with the ability to tailor the rigidity of the droplet interface (via surfactant concentration
in the continuous phase), the deformability of the inner phase (via gelation reactions), or the packing density (via osmosis, see below) (Figures S19–S21, Supporting Information).

2.5. Double Emulsions for Colloidal Supraparticles

Last, we demonstrate how our tailored double emulsions can provide superior confinements for the fabrication of functional materials, using the example of confined colloidal self-assembly. Recent years have seen the emergence of defined colloidal supraparticles, which are spherical assemblies of colloidal particles with collective properties that are distinct from both the individual building blocks and their bulk crystal analogues.\(^{[56,57]}\) The most common way to produce supraparticles is to encapsulate colloidal particles in a simple w/o droplet and subsequently remove the water from the confinement to trigger the self-assembly process. Hence, the droplet drying process itself plays a central role in determining the resulting supraparticle structure,\(^{[50,55]}\) which, in turn, determines the properties. Drying simple emulsions faces two challenges. First, the drying speed is typically controlled via temperature and storage conditions,\(^{[39,50,58]}\) and therefore lacks precision and cannot be stopped or restarted arbitrarily. Second, as the drying depends on the gradient of dissolved water in the continuous phase, the drying profile of each droplet differs, depending on its local position and environment. Thus, drying inevitably results in inhomogeneities between supraparticles within one sample. SCDE provides convenient and accurate control over the volume of the water core droplet via osmotic pressure.\(^{[59,60]}\) As the water core droplet and the continuous water phase are separated by a thin oil shell, the osmotic pressure in the two phases will equilibrate by diffusion of water molecules from the low-osmotic phase into the high-osmotic phase. When the osmotic pressure in the continuous water phase is higher, the water core droplet will shrink, otherwise it will expand. The volume change of the water core droplet can be controlled precisely, immediately, and dynamically by controlling the osmotic pressure in the continuous phase. We encapsulate polystyrene colloidal particles in double emulsion where SDS, present as surfactant during droplet production, acts as the active osmotic pressure agent in the continuous phase (Figure 5a).

The slow shrinkage of the water core droplet provides sufficient time for the confined self-assembly process to reach equilibrium, resulting in minimum energy crystal structures with characteristic anisotropic structural coloration patterns caused by icosahedral, decahedral, or fcc symmetries (Figure 5b).\(^{[10,61,62]}\) While only 70% supraparticles in simple w/o emulsion ever reach equilibrium even with slowest drying processes taking up to 40 days due to inhomogeneous drying,\(^{[50]}\) nearly all supraparticles in our double emulsion form defined crystal structures within a few days. The process can even be accelerated by applying high osmotic pressure for fast drying at the beginning and change to low osmotic pressure when crystallization begins.

The unique dynamic control of droplet drying allows expanding the water core droplet, which causes the melting of the colloidal crystal as the volume fraction reduces. As shown in Figure 5c, the color of the colloidal crystal first redshifts from blue to green (Figure 5c-i), indicating an increased distance of the particles...
within the crystal, and subsequently, the characteristic stripe patterns of the fcc crystal disappear,[61] marking the loss of structural order in the melting process (Figure 5c–iii), which finally result in a liquid phase with whitish appearance (Figure 5c–v).

3. Conclusion

We introduce a simple and scalable batch process to produce tailored double emulsions of various formulations at milliliter per minute rates, requiring only minimal experimental effort, expertise, and cost. Compared to conventional two-step emulsification methods such as stator rotator systems, our method produces SCDE with thin oil shell with a yield as high as 99%, without requiring microfluidic devices. We show that these properties arise from the unique emulsification mechanism that combines vortex-induced shear and density difference-induced friction. Conventional double-emulsification methods, where multicore droplets are randomly distributed within the entire continuous liquid medium, create a gradient of shear forces that decreases to zero at the container wall. Due to the small droplet dimensions, the shear force gradient exerted at an individual multicore droplet is often not sufficient for complete break-up into single-core droplets. In our case, as the heavier droplets are being pushed to the solid container wall by centrifugal forces during vortexing, they experience a large shear force gradient in the thin liquid film, which efficiently breaks up the multicore droplets. In addition, the friction at the solid wall removes excess liquid in the shell. The key for successful double emulsification is the density difference between the discontinuous droplets and the continuous phase. We demonstrate a w/o/w liquid system with a density difference between water and oil of 0.6 g cm$^{-3}$ and an o/w/o liquid system with a density difference of 0.14 g cm$^{-3}$. However, we note that the density difference between the discontinuous droplets and the continuous phase is much smaller, as the shell only consists of a small volume of the entire double-emulsion droplet (the droplet density is given by the mass of the droplet divided by the volume of the droplet, including cores and shell). As friction between the droplets and the solid wall removes liquid from the shell, the droplet density continuously decreases, creating a self-limiting process that converges the shell thickness to uniform and controllable dimensions. This mechanism also inevitably produces empty single-emulsion droplets by shearing off excess liquid in the shell, which could be removed in additional processing steps if required. We further demonstrate that our two-step emulsification method can be integrated to simple microfluidics to produce uniform double emulsions with wide range of droplet sizes. This provides the possibility to incorporate parallelized, high-throughput, single-emulsion-producing microfluidic devices for double-emulsion production. We anticipate our method to provide widespread access to tailored double emulsions as an enabling, versatile platform for fundamental research and the generation of advanced materials.

4. Experimental Section

Materials: Krytox surfactant (FSH 157) was purchased from Dupont. Sodium dodecyl sulfate, cetyltrimethylammoniumbromide, poly(vinyl alcohol), and Pluronic surfactant were purchased from Sigma-Aldrich. The fluorinated oil Novoc HFE 7500 engineering liquid was purchased from 3M. 15 mL and 50 mL centrifuge tubes were purchased from Carl Roth.

Double-Emulsion Production: All fabrication procedures are described in the main text and detailed in the Supporting Information.

Double-Emulsion Production with Microfluidics: For uniform double-emulsion droplets, single water-in-oil emulsion droplets were produced in a PDMS microfluidic drop-maker, following typical soft lithography methods as described in the literature.[19] In short, a silicon wafer was spin-coated with SU-8 negative photoresist, and a pattern mask was used to create microstructures on the coated water surface through UV light. The microstructures were then hardened and coated with an antisticking layer to produce the master wafer. PDMS (Sylgard 184 PDMS from Dow Corning) was mixed with curing agent at 1:10 weight ratio and degassed before pouring onto the master wafer for ~1 cm thickness. The PDMS was cured in 80 °C oven overnight. The cured PDMS chip was cut off by blazer and peeled off from the wafer. Biopsy punch (1.0 mm in diameter, Kai Group) was used to create the inlets and outlets in the PDMS chip. Chips with 2D flow focusing of 25 and 50 µm were used. A Scotch tape was used to remove debris and dust on the PDMS chip surface. The chip was washed by ethanol and water (Milli-Q) and dried with compressed air. After cleaning, the PDMS chip and a clean glass slide were plasma treated for 30 s in oxygen environment at 30 W power (Diener electronic, Femto). After surface activation, the PDMS chip was bonded to the glass slide and put in oven for 30 min to enhance bonding. Afterward, the microfluidics channels were immediately flushed with Aquapel (PPG industry) by injection through a 1 mL syringe of a flat-head suiting needle. After 1 h, the channels were flushed by compressed gas to remove the liquid and kept in oven to dry. Two syringes containing dispersed water phase and continuous oil phase were placed and pushed by a precision pump (Cronus) into the PDMS microfluidic device. Droplets and droplets as feed for double emulsions were produced at different combination of flow rates ranging from 50 to 500 µL h$^{-1}$ (water) and 50 to 200 µL h$^{-1}$ (oil).

Characterization: Droplets were characterized using an inverted transmission microscope (Nikon TS100) and a bright-field microscope (Leitz, Ergolux) in reflection mode with 10×, 16×, 20×, and 50× magnification objective lenses. Images of colloidal supraparticles were taken using a ZEISS Gemini 500 scanning electron microscope. N > 1000 droplets were measured for all data points.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This project was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 416229255 - SFB 1411. N.V. acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG) under project VO 1824/7-1 and support by the Interdisciplinary Center for Functional Particle Systems at FAU.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords
double emulsions, microfluidics, structural color, supraparticles, two-step emulsification

Received: September 15, 2021
Revised: October 22, 2021
Published online: December 6, 2021