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Mechanisms and control of single-step microfluidic generation of multi-core double emulsion droplets

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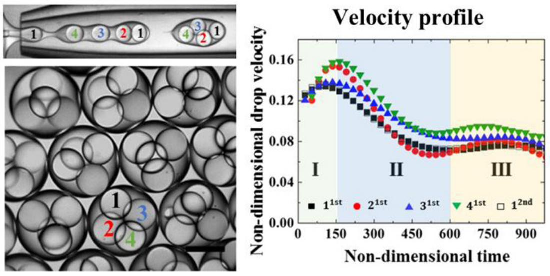
HIGHLIGHTS

- The mechanisms of single-step formation of multi-core double emulsion were revealed.
- Phase diagrams for predicting number of encapsulated inner drops were mapped out.
- The jet pinch-off process was accompanied and affected by presence of a vortex flow.
- The formation regime of inner phase affected the number of encapsulated inner drops.
- Large single-core capsules were made from dual-core drops with unstable inner drops.

GRAPHICAL ABSTRACT

Multi-core drop formation



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ABSTRACT

Single-step generation of monodisperse multi-core double emulsion drops in three-phase glass capillary microfluidic device was investigated using a micro-particle image velocimetry (micro-PIV) system. Phase diagrams were developed to predict the number of encapsulated inner drops as a function of the capillary numbers of inner, middle and outer fluid. The maximum stable number of inner drops cores in uniform double emulsion drops was six. Starting from core/shell drops, the formation of double emulsion drops with multiple cores was achieved by decreasing the capillary number of the outer fluid and increasing the capillary number of the middle fluid. A stable continuous jet of the middle fluid loaded with inner drops was formed at high capillary numbers of the middle fluid. Empirical correlations predicting the size and generation frequency of inner drops as a function of the capillary numbers and the device geometry were developed. Dual-core double emulsion drops were used as templates for the fabrication of polymeric capsules using "on-the-fly" photopolymerisation. The capsule morphology was controlled by manipulating the stability of the inner drops through adjusting the concentration of the lipophilic surfactant in the middle fluid. At low concentration of the lipophilic surfactant, inner drops coalesced during curing and single compartment capsules with thin shells were produced from dual-core drops. The core/shell capsules produced from multi-core drops were monodispersed and larger than those produced from core/shell drops in the same device.

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1. Introduction

Multi-core double emulsions are complex emulsions composed of several inner drops dispersed in an immiscible middle phase, which is itself dispersed in the outer phase. They can be used for encapsulation of multiple reactive components for triggered reaction and mixing [1–3], co-culture of multiple cells in cell-based therapies [4], encapsulation and sequential release of incompatible active materials and liquids while avoiding cross-contamination [5], and the production of multi-compartment capsules [6]. Conventionally, multiple emulsions are produced in two consecutive emulsification steps through high-shear mixing of immiscible liquids [7]. However, this approach is associated with broad particle size distribution, low batch-to-batch reproducibility, low encapsulation efficiency, high energy consumption, and a lack of control over the size of the drops and the number of encapsulated inner drops [8,9].

Microfluidic emulsification is a promising tool for reproducible production of monodispersed multiple emulsion drops of versatile morphology [5,10–12]. Multi-core drops are usually produced using two consecutive T-junction [8,13], co-flow [10,11,14–16], and flow-focusing [17,18] drop makers. Perro et al. [16] used two consecutive co-flow makers made of fused silica capillaries to produce structured polymersomes and map out phase diagrams predicting the number of inner drops as a function of fluid flow rates. The number of inner drops decreased as the outer and middle phase flow rates increased. Okushima et al. [13] used two consecutive T-junctions made on a Pyrex glass to produce double emulsion drops with a controlled number of inner drops. The number of inner drops was found to increase with increasing flow rate of the inner phase. Using a two-step microfluidic device composed of three coaxial glass capillaries, Kim et al. [11] observed that the number of inner drops increased with increasing middle-to-inner volumetric flow rate ratio. Chu et al. [10] derived an empirical equation to predict the number of inner drops in multi-core droplets produced in a glass capillary device consisting of two consecutive co-flow drop makers. The number of inner drops was reduced by increasing the outer phase flow rate.

In the two-step emulsification approach, the generation of inner and outer drops is spatially separated; thus, synchronising the frequency of drop generation at different steps requires delicate control of individual flow rates [5]. Single-step microfluidic emulsification methods [6,19,20], e.g., a combined co-flow and counter-current flow focusing (Fig. 1a) [21], in a three-phase glass capillary device, can overcome this disadvantage, since the flow rates of the inner and middle fluid do not need to be synchronised. Moreover, one-step processes are advantageous for very thin-shelled core/shell drops, which are difficult to create in a two-step process. In addition, the capillary device for single-step emulsification is easier to fabricate than the device composed of two sequential drop generation units [10,15], due to simpler design and smaller number of capillaries and connectors [6,22].

Three main regimes of double emulsion generation in three-phase glass capillary devices are dripping, widening jetting, and narrowing jetting. In the dripping regime, highly uniform drops are formed near the orifice of the collection tube, while widening and narrowing jetting are associated with the production of polydispersed large and small drops, respectively, further downstream of the orifice [23,24]. For highly uniform multi-core drops, the cores should be formed in the dripping regime and the outer drops in the dripping-to-widening jetting transition regime [6]. Lee et al. [6] used a three-phase glass capillary to produce nonspherical colloidosomes. The higher inner and middle phase flow rates and the lower outer phase flow rates favoured encapsulation of larger numbers of inner drops. Although Lee et al. [6] briefly reported the effect of flow rates on the number of encapsulated inner drops, however, the mechanism of single-step formation of multi-core double emulsion drops has not yet been fully understood and needs to be investigated.

The purpose of this work is an in-depth investigation into the mechanisms of single-step generation of multiple emulsion drops in a co-flow/flow focusing microfluidic geometry. Novel phase diagrams have been developed to depict the effect of capillary numbers of the inner, middle, and outer fluids on the number of inner drops, and determine the operating conditions for successful production of double emulsions. The flow field during jet pinch-off was visualised by seeding charged latex beads in the outer phase. The generated drops were used as templates to produce capsules with controlled number of compartments via "on-the-fly" photopolymerisation. The number of cores in the capsule was controlled by manipulating the stability of inner drops during curing by varying the concentration of lipophilic surfactant in the middle

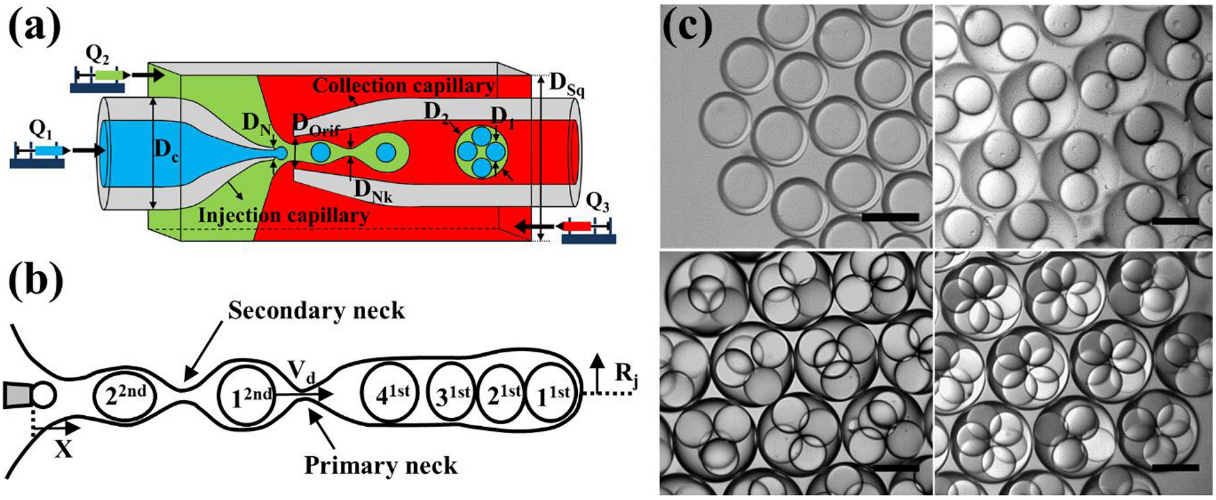

Fig. 1. (a) A schematic of the microfluidic device used in this work: Q_1, Q_2, Q_3 = flow rates of inner, middle and outer phase, D_1, D_2 = diameters of inner and outer drop, D_{sq} = inner width of square capillary, D_c = outer diameter of the injection tube, D_N, D_{orif} = orifice diameters of the injection and collection tube, D_{Nk} = neck diameter; (b) Schematic of a middle phase jet with the primary and secondary neck (V_d = velocity of the 1^{2nd} inner drop); (c) Optical images of the generated drops composed of one, two, four, and six inner drops. All scale bars are 500 μm.