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RESEARCH PAPER

Generation of Water-In-Oil-In-Water (W/O/W) Double Emulsions by Microfluidics

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Abstract: Novel compartment microparticles prepared with double emulsion droplets as templates provide a protected internal space for material encapsulation. The effect of three-phase flow rate on the micro-droplet generation of double emulsion mechanism is available for reference to produce precise size and highly monodisperse particles. The influence of three-phase flow rate on the formation mode and size of the emulsion droplets is investigated by combination of experiment and numerical simulation. The size of compound droplets decreases and frequency increases with the increasing outer fluid flow rate. The monodispersity of the double emulsion reduces due to transition from dripping to narrowing jetting regime. Outer droplet size increases with the increasing flow rate of the middle fluid, whereas inner droplet size is the opposite. The frequency increases and then stabilizes, which leads to a widening regime. When $Q_2/Q_1 > 6$, the multi-core type double emulsion droplets are produced. Droplet coalescence occurs when surfactants is not involved. As Q_1 increases, there is an increasing tendency for inner drop size. The outer drop size is proportional to the sum of the inner and middle flow rate, and that is irrelevant to Q_1/Q_2. For drop size, the ratio of core-shell and internal structure is precisely controlled by adjusting three-phase flow rate respectively.

Key Words: Microdroplet; Double emulsions; Cow-flowing; Numerical simulation

1 Introduction

Double-emulsion droplets are composed of a droplet dispersed in a lager incompatible droplet, which have been used as templates to produce core-shell[1], hole-shell[2] and multi-compartment microparticles[3] in drug delivery and controlled release, encapsulation of active material[4], chemical catalysis and biochemical separation and other fields[5]. The performance of the prepared material mainly depends on the structure of the double emulsion droplets. Therefore, the stable and high-speed formation of monodisperse double emulsion droplets is the key to its application. The drops are monodisperse, homogeneous and spherical, which have high controllability and raw material utilization[6–10]. 2D microchannel structures such as two-stage T-type[11] or cruciform[12] are difficult to precisely control the wettability of the device. Therefore, glass capillary based on 3D microfluidic systems are widely applied in the synthesis of double emulsion droplets.

For the first time, Utada *et al*[7] used a co-flow microfluidic device to generate monodisperse double emulsions by one step, and investigated the influence of the outer flow velocity on its size. In their work, the inner phase and the middle phase were sheared by external solution simultaneously so that droplet encapsulation was relatively good. In addition, the capillary surface modification could be suitable for high viscosity organic solution on the double emulsion drops with ultra-thin shells[8]. Chu *et al*[9,10] presented a highly scalable micro-capillary technique that simultaneously controls the droplet monodispersity as well as the number and size of the inner droplets. Shao *et al*[13] designed a coaxial micro-device that could be easily assembled and disassembled. The mechanism was proposed to explain the significantly different phenomenon brought about in one-step and two-step devices.

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The application of numerical analysis method effectively promote the study on the formation of double emulsions[14–18]. Zhou *et al*[14] numerically studied the formation of double emulsions in 2D micro flow-focusing devices and analyzed the effect of liquid viscosity on the droplets formation in Dripping and Jetting regime. Vu *et al*[15] used front-tracking/ finite difference method to investigate breakup modes of an axisymmetric, laminar compound jet of immiscible fluids, which flows in a co-flowing immiscible outer fluid. Otherwise, the volume of fluid method can effectively predict the deformation and fracture of the double emulsions under the action of shear flow, and the mutual conversion between flow patterns[16].

Although there are obvious advantages in the preparation of functional microparticles based on coaxial flow technology, most of the researches on these devices focus on the generation of double emulsions in different way and application at present[17–23]. However, relevant mechanism study and parametric analysis are less, especially the study on flow conditions for generation of double emulsions in capillary microchannel and the analysis of change rule of droplet size with flow rate[17,18]. In this study, we investigated the double emulsion formation in three-phase coaxial capillary device by combination of experiment and numerical simulation, mainly focused on the influence of three-phase flow rate on the generation pattern, frequency and size of the emulsion droplets.

2 Geometric model

The model adopted in this study draws on the co-flowing microchannels of gas-in-oil-in-water double emulsion droplets studied by Chen *et al*[24]. To generate smaller droplets, circular capillaries tips of the inner phase, middle phase and collecting tube are tapered. Figure 1 shows the microfluidic chip device, schematic diagram and schematic of simulated mesh. The co-flowing microchannel structure mainly comprises three layers of nested capillaries. The inner and outer diameters of circular capillaries of the inner phase are 0.10 and 0.17 mm respectively, and the tip is stretched to diameter of 0.05 mm. The tube with inner and outer diameters of 0.58 and 1.00 mm and tip diameter of 0.4 mm is used as the middle phase channel and collecting channel. Outer phase square channel is 1.05 mm in inner width and 1.5 mm in outer width. In addition, the outer surface of the inner phase channel and the inner wall of the middle phase channel were treated with octadecyltrichlorosilane (OTS, Sigma-Aldrich) to make them hydrophobic. In numerical calculation, the model is an axisymmetric model, so half of the central axis plane is meshed and calculated (Fig.1C).

3 Experimental device and method

3.1 Experiment devices

VEO340 high-speed camera (Phantom, USA) was used to capture and observe the water-in-oil-water (W/O/W) double emulsion droplets in the three phases co-flowing microchannels. Experimental devices include fluid control system and image acquisition system, as shown in Fig.2. The fluid control system uses an 11Elite syringe pump (Harvard, USA) to inject the three-phase fluid through the PTFE tubing into the microchannel inlet. The IX73 microscope (Olympus Corp., Japan) has a magnification of 10 times and uses high-speed photography to capture images of the flow in the microchannel at 800 frames per second.

3.2 Materials

The entire experimental process was carried out at room temperature (20 ºC) and atmospheric condition. The internal aqueous phase was composed of 5% (*w*/*w*) glycerin (Sinopec Chemical Reagent) and 95% (*w*/*w*) deionized water. The middle oil phase consisted of a mixture of silicone oil (50cSt,

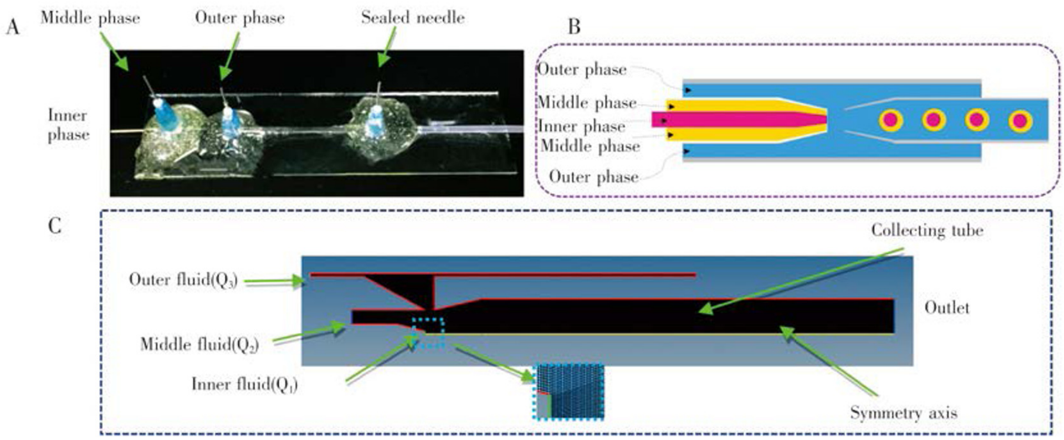

Fig.1 Microfluidic chip structure diagram for synthesis of double emulsion droplets: (A) glass capillary microfluidic device; (B) schematic illustration of double emulsion generation process; (C) schematic of simulated mesh