FULL PAPER

One-step microdevices for synthesizing morphology-controlled ultraviolet-curable polysiloxane shell particles

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Abstract

Double emulsions have great potential application in many fields. Although many companies and research institutions have developed various strategies for forming double emulsions, production and stability are not straightforward. Meanwhile, none of the well-organized simple device and scalable technique was available to form highly monodispersed double emulsions. Herein, we present a one-step strategy to produce highly monodisperse double emulsion via assembled micro-cross device. This device has a lot of advantages, such as easy assembly/disassembly and high repeatability. High-throughput is also easily achievable for its high-pressure capacity. Moreover, we systematically studied the effects of the three flow rates on the size and structure of the double emulsions. A mathematical model has been developed to predict the inner and outer droplets size of the double emulsion. We prepared the flame-retardant microcapsules with a dimethyl methylphosphonate (DMMP) inner core and an ultraviolet-curable polysiloxane shell. We hope that this assembled micro-cross device can be employed extensively in the area of microfluidics.

Keywords Microcapsule · Microfluidic approach · One-step · Three-dimensional micro-cross · Flame-retardant

Introduction

Multiple emulsions are complex multiphase systems in which dispersed droplets contain smaller droplets inside [1–4]. For a double emulsion, it is a system in which the dispersed droplets can encapsulate the active molecules in the internal aqueous phase. Thanks to their advantageous and controllable retention ability [5, 6], it is widely used in chemical reactions, drug delivery, micro-sized functional cargo [7–14]. For all these applications, it is crucial that generating and controlling single/double emulsions with various sizes and the stability.

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In previous research, there were two different methods to generate double emulsion, known as "one-step" and "two-step" processes [2, 3, 15]. Double emulsions are most often formulated by means of a "two-step" processes. For this method, the inner emulsion is produced at first. In the second emulsification step, this W/O emulsion forms the dispersed phase of the double emulsion. During this step, the droplet size distribution of inner water droplets and the amount of water encapsulated in the oil droplets can be influenced [16]. However, in these two-step approaches, there is a very large disadvantage. Because of the unsteady flowing condition in the second stage, which may affect the formation inner emulsion at the first stage, it is difficult to control the flow [17, 18]. In contrast, "one-step" method has two advantages (1) simplicity: only one set of mixing conditions has to be optimized (2) robustness: the second mixing step does not make the first mixing step unstable [3].Therefore, there are currently many microfluidic devices and fabrication methods for "one-step" double emulsion formation [19–21]. However, for "one-step" method, no simple controlled device and scalable technique has been achieved to formation high monodisperse double emulsions.

Recently, increasing attention has been attracted by microfluidics. It has been a new method to produce microbubbles and monodispersed droplets with controllable structures

[22–24].Microfluidics also showed remarkable capabilities for preparing double emulsion. Such as polydimethylsiloxane (PDMS) through soft-lithograph, glass capillary devices and glass etching are wonderful methods enable precise preparation for one-step emulsions. Abate et al. use PDMS device to present a robust way. This way can create multiple emulsions which can be broken into double emulsions in one-step by adjusting flow rates [25]. Wang et al. report a simple one-step capillary microfluidic device with a "double co-flowing" geometry that can achieve the steady formation of gas/liquid/liquid double emulsions [26]. However, PDMS microchannel require high level clean, complex progress and long fabrication time. For conventional glass capillary microfluidic devices, because of handmade processes, it is difficult to strictly repeat the experimental results [27]. At the same time, those devices are limited to the bonding method, and it is difficult to apply in the high-pressure and high-throughput systems. More than the type of microfluidic devices, the surface wetting properties also play an important role on the formation of double emulsions. In essentially hydrophobic microchannels, W/O droplets can be easily achieved while stable formation of O/W droplets is very difficult. By selectively modifying the surface properties of certain areas of the PDMS device, Bauer et al. developed the layer-by-layer approach to successfully generate W/O/W double emulsions [28]. Besides, three-dimensional (3D) flow focusing is a feasible method to avoid wetting problems as the dispersed phase can't contact the channel surfaces by the surrounding continuous phase. Huang et al. utilized three layers of SU-8 resist structures to present a planar 3D flow-focusing device with coaxial orifices and produced single/double emulsions [29]. But surface modifications and fabrication process are difficult and time consuming processes. For 3D structures microfluidic device may lead to expensive cost and intricate operations, which make it difficult in industrial production. Recently, some "off-the-shelf" devices are successfully used in some microfluidic experiments. In our previous study, droplets production and fission have been excellently implemented using commercially available components [30, 31]. What's more, it can effectively solve the problem of hydrophilic and hydrophobic on the 3D structure. These devices are easily assembled/disassembled in a short time. High-throughput is also easily achievable for its high-pressure capacity. Furthermore, another advantage is that it can be easy to connect with other equipment for subsequent analysis due to the capillary outlet [32].

Herein, we present a simple one-step way to produce high monodisperse double emulsion via three-dimensional micro-devices. By making a little adjustment with three-dimensional micro-devices. We are injecting a smaller capillary into another PEEK tube to make the tapered orifices align where the single emulsification carries on. It can reduce the distance of the two-dispersion stage to a degree that the interference between them flowing conditions can be eliminated. We demonstrate the high reliability of these devices to form monodisperse single and double emulsions with flexibly controlling droplets size. Moreover, we systematically studied the effects of the three flow rates on the size and structure of the double emulsions. A mathematical model is developed to predict the inner and outer droplets size of the double emulsion. On this basis, we prepare the flame-retardant microcapsules with a dimethyl methylphosphonate (DMMP) inner core and an ultraviolet-curable (UV-curable) polysiloxane shell.

Experimental

Device configuration

The configuration of this microfluidic droplet generator is comprised of a cross (Dalian Xinsheng Hardware, China), four adapter and capillaries. The material of the cross body is stainless steel. As drawn in Fig. 1a, we insert the glass capillary tubes (OD 360 μm, ID 150 μm) through the adapter into the cross, then fingering tighten securely. At end of the inner phase capillary is taper with the aid of a laser-cutting instrument (Sutter instrument Company, Micropipette Pullers, Model P-2000). With the help of ceramic cutting, one can also have an orifice of a desire size by cutting the capillary tip by a proper size. For the single emulsion device, the size of orifice is 60 μm. In the double emulsion device, we use an adapter that has a connection at both ends to connect the two crosses (Fig. 1b). A peek tube (OD 800 μm, ID 600 μm) which is the flow channel of the intermediate phase be install inside of this adapter. Outlet capillary with inner diameter 150 μm and the diameter of orifice is 80 μm. The detailed structure and internal geometrical dimensions of the cross-section of the device are illustrated in Fig. 1c, d. Both micro-crosses and glass capillary tubes are easily reusable for implementing droplet generation. For microfluidic droplet generating device, it is always accompanied by high pressure during work. For this cross, it is used for connecting capillaries in high-throughput and high-pressure machines of biological detection/screening. Therefore, this cross can withstand fluid pressure up to 275.6 bar. Moreover, we can disassemble these individual components and clean them by alcohol or ultrasound, then dry them by nitrogen, finally reassemble them for reutilization, which reduces the cost significantly.

Fluid manipulation

For fluid manipulation, the most important is to find a proper surfactant to prevent the droplets from merging or breaking up while lowering the interfacial tension of the two phases. To verify the feasibility of this one-step micro-device, we chose a fluoride surfactant, which is 0.05% Triton X-100 (T9284, Sigma) and 2% ABIL EM90, along with mineral oil (#M-3516, Sigma) as the middle phase. As shown in Fig. 1c,
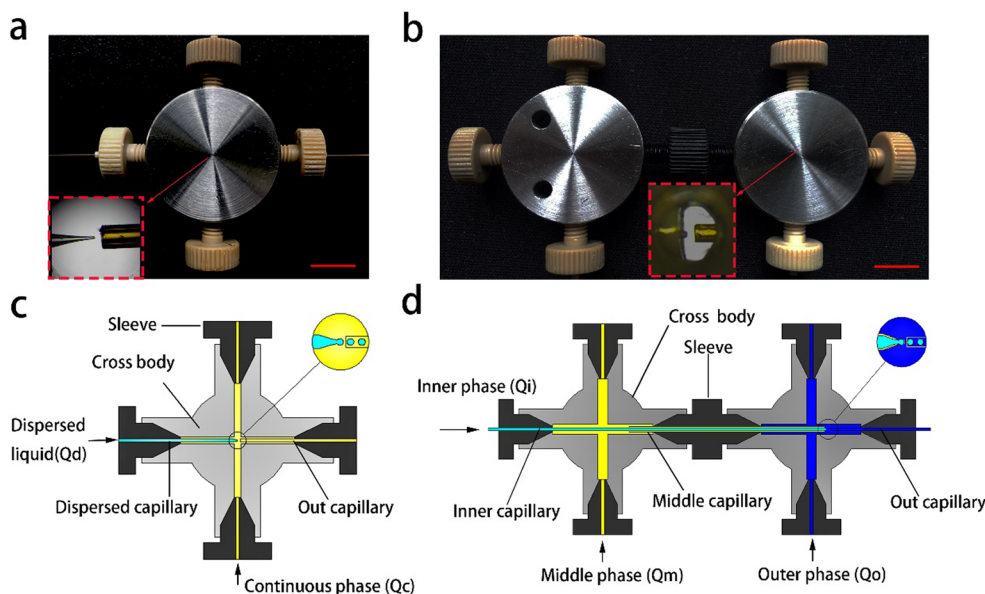
Fig. 1 Photograph and schematic drawing of the microfluidic devices used for the production of single (a,c) and (b,d) double emulsion. **a** The assembled micro-devices connected to capillary tubing with 360 µm OD. **b** A peek tube (OD 800 µm, ID 600 µm) which is the flow channel of the intermediate phase be install inside of this adapter. The cross-sectional view of the micro-devices, in which the channels are all three-dimensionally axisymmetric. **c** Q_d and Q_c denote the flow rate of the dispersed liquid and the continuous liquid, respectively. **d** Q_i, Q_m and Q_O denote the flow rate of the inner phase, middle phase and the outer phase, respectively. Scale bar is 1 cm

continuous phase liquid (Q_c) is injected symmetrically from two inlets and dispersed liquid (Q_d) enters from another, with the last tube acting as an exit. At the location of the cross junction, the dispersed liquid is hydrody-namically focused to form a tip and eventually breaks up into droplets due to natural instability. In order to produce the flame-retardant microcapsules, the inner and middle phase fluids were prepared by adding 2-wt% dyeing agent and Span 80 to the DMMP solution, adding UV-curable polysiloxane with 2-wt% Span 80, respectively. For the outer phase we use deionized water contains glycerol (15-wt%), with plutonic F-127 (2-wt%). A set of HPLC solvent delivery systems (ABI 140D solvent delivery system, USA) was used for pumping, with a flow rate as precise as 1 nL/min. The relevant physical parameters of the liquids used in this work are listed in Table 1. We measure viscosities through a high precision viscometer (SYD-256H, Shanghai, China).

Table 1 Summery of physical parameters of the liquids

| Phase	Liquid
Inner phase 1	Deionized water
Inner phase 2	Dimethyl methylphosphonate + 2 wt% dyeing + 2 wt% Span 80
Middle phase 1	Mineral oil + 0.05 wt%Triton X-100 + 2% wtABIL EM90
Middle phase 2	UV-curable polysiloxane + 2 wt% Span 80
Outer phase	Deionized water + 15% wt glycerol + 2%wt F-127

Results and discussion

Preparation of monodisperse W/O and O/W emulsions

In order to verify the feasibility of this droplet generator, we use a single cross to produce W/O and O/W emulsion with desired sizes. The droplet sizes and frequency can be controlled by adjusting the flow rate as reported. To verify the effects of the flow rate on the droplet size in this cross, we keep the dispersed phase (deionized water) flow rate Q_d at 2µL/min, 5µL/min, 10 µL/min respectively, then increase the continuous flow rate, highly uniform water droplets can be obtained as shown in Fig. 2a, b. The coefficient of variance (CV) of the single W/O emulsions is less than 2.2%, it is a commonly accepted definition of monodispersed with CV of less than 5%. Alternatively, we can also get homogeneous oil droplets when mineral oil acts as the dispersed phase, as illustrated in Fig. 2c, d. The CV of the single O/W emulsions is about 3.1%, meaning that oil droplets are also highly well distributed. Though these droplets are so closed to each other, they are not coalescence mainly because of the F-127 surfactant seems to form a much thicker membrane around the oil droplet surface. In conclusion, this device without any treatments can produce not only W/O emulsion but also O/W emulsion excellently.

As shown in Fig. 3a, we can find that if the dispersed phase flow rate is constant, the droplet diameter is inversely proportional to the flow rate ratio q. Though flow rate ratio q is the same, higher dispersed phase flow rate means smaller droplet diameter. In addition, while dispersed phase and continuous

Fig. 2 **a** Highly uniform W/O emulsions. **b** Water droplets in capillary tube. **c** Highly uniform O/W emulsions. **d** Oil droplets in capillary tube. Scale bar is 150 μm for (a) and (c). Scale bar is 100 μm for (b) and (d)
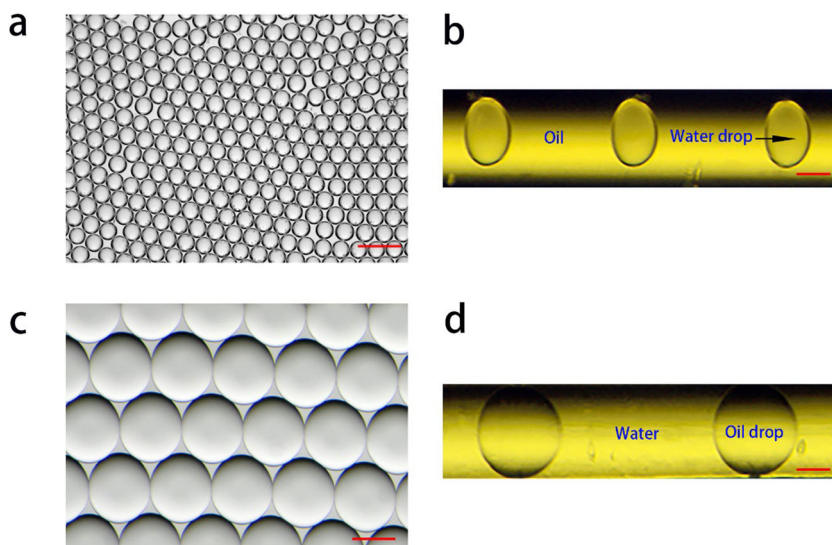
phase flow rates are the same, W/O droplet size is smaller than O/W droplet size. Usually, the dominant mechanism varies with the capillary number of the continuous phase:

$$Ca = \frac{u_c \mu_c}{\gamma} \qquad (1)$$

Where u_c and μ_c are the velocity and viscosity of the continuous phase respectively, γ is the surface/interfacial tension, the droplet size is primarily determined by capillary number (Ca).

In this case, viscosity ratio($\alpha = \mu_c/\mu_d$) is the only different factor in the droplets generation process, where μ_c and μ_d are defined as the viscosity of the continuous phase and the dispersed phase respectively. The increase of the viscosity ratio, 24.28 for W/O droplet and 1.22 for O/W droplet, results in smaller diameter of the droplets due to the relative increase in the cross-flow shear force over the interfacial force at the cross, which is consistent with previous works about the effect of viscosity. In the process of droplet generation, what we have interest in is not only the size and uniform of droplets, but also the generation frequency. We calculate the frequency f according to the equation: $f = Q_d/V_d$. The droplet volume V_d is obtained from the formula $V_d = \pi d_d^3/6$ and d_d is the mean droplet diameter. As shown in Fig. 3b, when the dispersed phase flow rate Q_d is constant, the droplet generation frequency increases with the increasing of the flow ratio q for both W/O emulsions and O/W emulsions. In the same flow ratio, the higher dispersed phase flow rate is accompany by the higher frequency. Many researchers have done the work about the droplet generation frequency. In micro-channels based-PMMA, Nisisako et al. generated W/O droplets at a frequency of up to 2500 per second [33]. By utilized microfluidic devices based on microscope glass slides and cover slips, Deng et al. produced W/O droplets at a frequency of more than 1000

per second [34]. It should be noted that the frequency of droplet formation in our cross can reach at least 6000 per second. Even though in such a high speed, the cross is still intact and all droplets are highly monodisperse. These features indicate that the device shows excellent performance for extremely high throughput of single droplet production.

Formation of monodispersed W/O/W double emulsions

Based on the successful utilization of the cross for producing highly monodisperse single W/O and O/W emulsions, further exploration to produce W/O/W double emulsions has been investigated. With this one-step emulsification method, we can get highly uniform W/O/W emulsions. Figure 4 shows a representative sample of the hexagonal close-packed monolayer adopted by the double emulsion droplets on glass slides. Both inner and outer droplets size are regular. Moreover, the double emulsions, consisting of single internal droplet with the same diameter and outer droplet with different diameter, can be easily obtained. Figure 4b and c show two typical micrographs of highly monodisperse W/O/W double emulsions, which have the same size of the inner droplet but different sizes of the outer droplet. Both the mean diameter of the inner droplets in Fig. 4b and c is 76 μm with CV of 3.2%, while the mean diameter of the outer droplets is 165 μm with CV of 3.1% for Fig. 4b and 210 μm with CV of 2.5% for Fig. 4c. As we set the Q_i =4μL/min, Q_m =6μL/min and Q_O = 120μL/min, this allows double emulsions to be formed with thin shells Fig. 4d1. Adding fluorescent reagent to the inner phase for a clearer observation of the package effect Fig. 4d2.

As we can see from the Fig. 5a and b shows that while keeping other parameters fixed, the inner droplet diameter increase with the inner phase rate (Q_i) and decreases while increasing the flow rate of the middle phase (Q_m). In general,
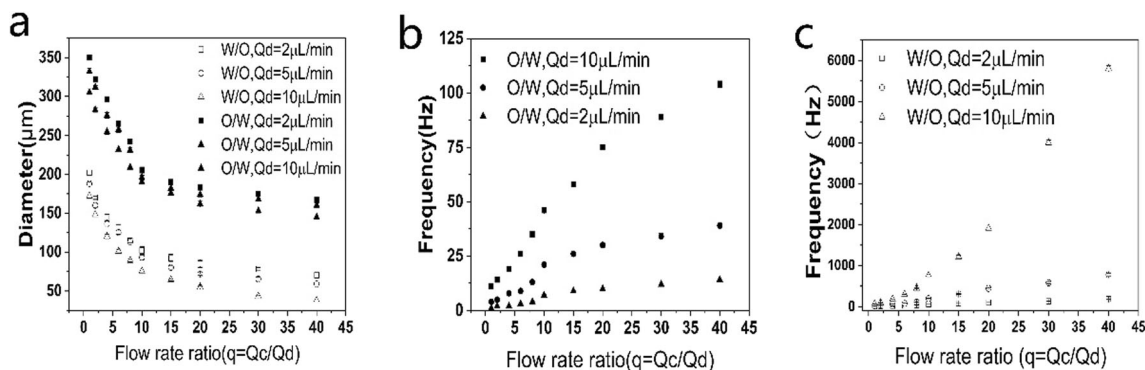
Fig. 3 (**a**) W/O and O/W droplets size versus flow rate ratio at different dispersed phase flow rate. Relationship between the droplet generation single W/O emulsions (**b**) and O/W emulsions (**c**) frequency f and flow rate ratio $\frac{Q_c}{Q_d}$

if the inner phase flow rate and middle phase flow rate are fixed, the internal droplet diameter di is almost constant, which has nothing to do with the outer phase flow rate as show in Fig. 5c. The increase of the inner phase flow rate leads to the increase of the pressure, resulting in the increase of the size of the droplet to reach the Laplace balance. As the increase of the middle phase, the drop formation related to the interfacial tension and the viscous shear force, the higher middle phase flow rate leads to higher viscous shear stress, leading the decrease of the drop size to obtain the balance. Owing to the outer phase has no relationship to the balance, the inner droplet size has nothing to do with the outer phase flow rate.

Furthermore, we also consider the effects of the flow rate on the outer droplets. As show in the Fig. 5d, with the increase of the inner phase flow rate, there is not much change in the outer droplet size. For this microfluidic device, the drop formation involves a balance between the interfacial tension and the viscous drag imposed by the flow of the surrounding fluid. The inner phase flow rate can be negligible as compared with the middle phase, so it does not have much effect on the balance. On the other hand, the size of the outer drop increase with the increase of the middle phase and decrease of the outer phase rate. Figure 5e, f. Due to the influence of the middle and outer phase on the Laplace pressure and the effects of the outer phase flow rates on the viscous shear force. Therefore, we can get the desired double emulsions with fixed inner droplet diameter and various outer droplet diameters just by adjusting the external phase flow rate.

The scaling laws on the control double emulsions

The results given in above indicate that if the outer phase flow rate Q_O and the internal total flow rate ($Q_m + Q_i$) are fixed, the

Fig. 4 Highly monodisperse W/O/W double emulsions with one singe water droplet in oil droplet. (a,b) They have the same outer diameter but different inner diameter. Both the outer phase flow rate Q_O =80μL/min, while Q_i =2μL/min, Q_m =32μL/min in (a) and Q_i =4μL/min, Q_m =28μL /min in (b). (b,c) They have the same inner diameter but different external diameter. Both the inner phase flow rate Q_i =4μL/min, the middle phase flow rate Q_m =28μL/min, but the outer phase flow rate (b) Q_O =80μL/min and (c) Q_O =35μL/min. (d) As we set the Q_i =4μL/min, Q_m =6μL/min and Q_O =120μL/min, this allows double emulsions to be formed with thin shells. Scale bar is 200 μm
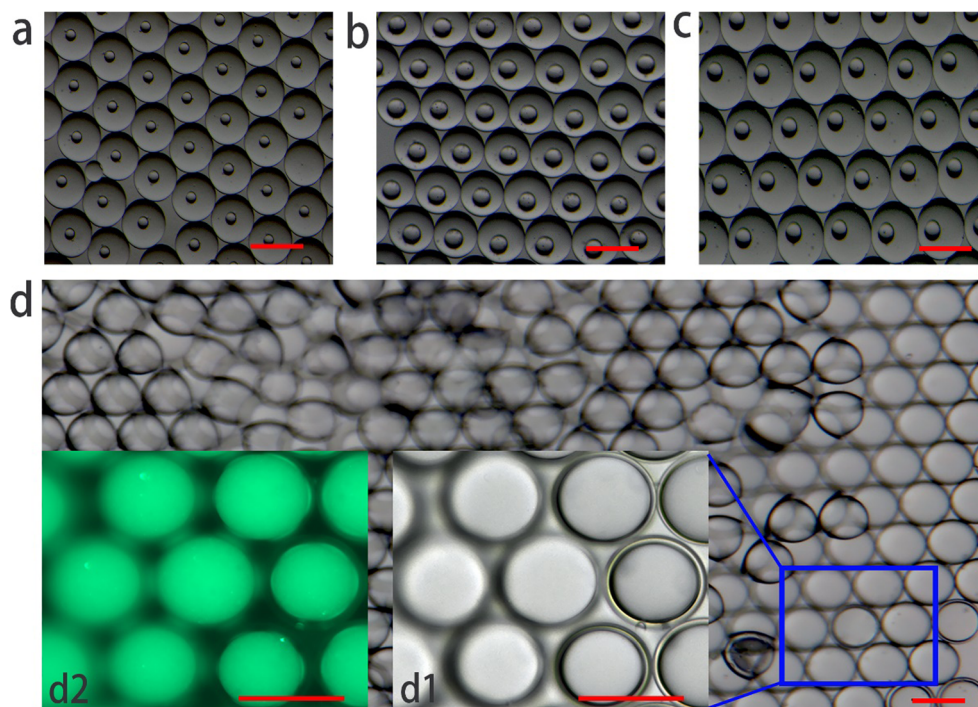
Fig. 5 The influences of the three phases flow rates on the inner and outer drop size. (a) The effect of the inner phase flow rate on the inner drop size (Q_m =10μL/min, Q_O =80μL/min).(b) The effect of the middle phase flow rate on the inner drop size (Q_O =80μL/min, Q_i =1,2,4μL/min respectively).(c) The effect of the outer phase flow rate on the inner drop size(Q_i =1μL/min,Q_m =9μL/min).(d) The effect of the inner phase flow rate on the outer drop size(Q_m =10μL/min,Q_O =80 μL/min). (e) The effect of the middle phase flow rate on the outer drop size (Q_i =2μL/min,Q_O =80μL/min). (f) The effect of the outer phase flow rate on the outer drop size (Q_i =1μL/min,Q_m =10 μL/min)
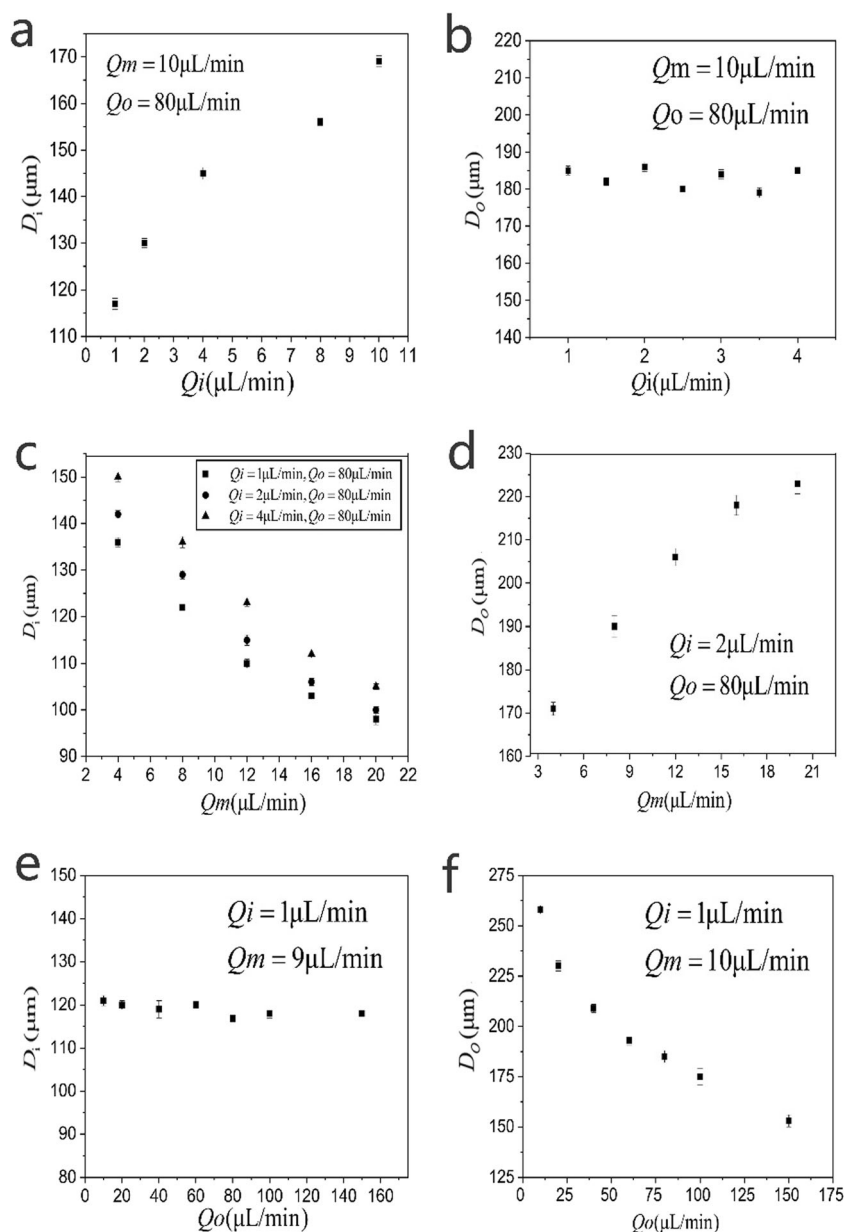
external droplet diameter Do is almost constant with different values of the inner phase flow rate Q_i to the sum (Q_m +Q_i), while the inner droplet diameter di is determined by the inner flow rate ratio Q_m /Q_i. Therefore, the droplet size is directly influenced by the Q_i,Q_m and Q_O.

In the previous work, a dimensionless number, capillary number (Ca), is used to describe the competition between the viscous shear force caused by the continuous phase and the surface tension/interfacial tension. Based on the scaling laws on the formation of micro-droplets in co-flowing microfluidic device, the droplet size can be presented by the following equations:

$$\frac{D_i}{d_i} = k_1(Ca)^\alpha \left(\frac{Q_i}{Q_m}\right)^\beta \tag{2}$$

$$\frac{D_o}{d_m} = k_2(Ca)^\alpha \left(\frac{Q_i + Q_m}{Q_O}\right)^\beta \tag{3}$$

In the fixed microfluidic device,k_1 and k_2 are constants, d_i and d_m are the diameters of the orifice of the first and middle capillary respectively.α and β are the indexes of the Ca and the phase ratio. By correlating the experimental results, we have:

$$\frac{D_i}{d_i} = 4.84\left(Ca\right)^{-0.12}\left(\frac{Q_i}{Q_m}\right)^{0.1613} \tag{4}$$

$$\frac{D_O}{d_m} = 2.195\left(Ca\right)^{-0.05}\left(\frac{Q_i + Q_m}{Q_O}\right)^{0.1768} \tag{5}$$

Fig. 6 Comparison of experimental data with the calculated results of the models. The predicted results fit very well with the experimental data
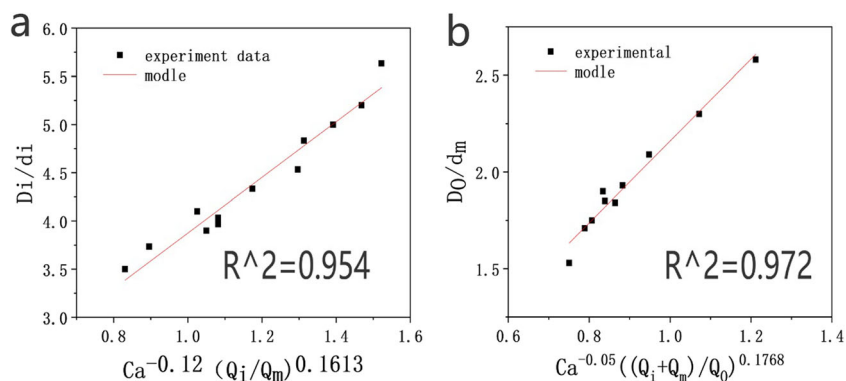
The comparisons of experimental data with the correlated results are given in Fig. 6a and b, which show the predicted results fit very well with the experimental data.

Preparation of flame-retardant microcapsules

Dimethyl methylphosphonate (DMMP) is a very effective water-soluble liquid flame retardant [35, 36]. In a premixed flame, DMMP was found to be very effective in reducing the burning velocity, which is approximately 141 times (on a molar basis) CO_2 [37, 38]. Microencapsulation is a protection technology that isolates the core material from the surrounding environment, which can avoid its reaction, volatilization, and deterioration [39, 40].

Based on the controllable production of flame-retardant microcapsules in this one-step device. Preparation of monodisperse microspheres includes two processes, one is the generation of the W/O/W double emulsion droplet and the then exposed to UV irradiation for around 10 s which initiated the polymerization reaction at the interface to form a thin shell covering the inner phase. The DMMP solution, the UV-curable solution, and the glycerol aqueous solution were prepared as the inner, middle,

and outer phase fluids of the W/O/W double emulsion, respectively. The Fig. 7a-c show the optical micrographs and Fig. 7d-f scanning electron microscope (SEM) images of microcapsules. We can see that the flame-retardant microcapsules are in the good spherical shape and with different structures by tuning the three flow rates. We find some gaps in a few droplets as show in Fig. 7c, f. If droplets that do not solidify immediately may cause the inner layer of droplets to sink to the bottom. When solidified, broken pores appear, and the thickness of the wall is nanoscale. It possible that this microcapsules structure can be applied with drug release in the future.

Conclusions

In summary, we describe a new technique, based on commercially available components that can readily be taken apart and cleaned between uses. We demonstrate the performance of the assembled cross for formation of monodisperse single emulsion and production of highly monodisperse double emulsions in one-step way. We systematically studied the effects of the three flow rates on the
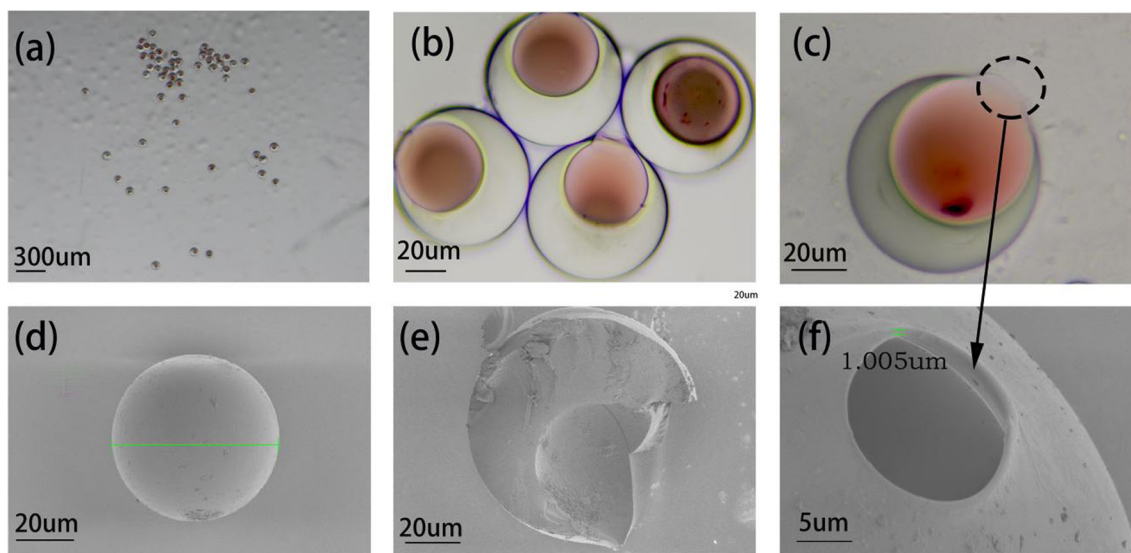

Fig. 7 (**a-c**) optical micrographs of flame-retardant microcapsules. (**d-f**) field-emission scanning electron microscope (FE-SEM) images of microcapsules

size and structure of the double emulsions. A mathematical model is developed to predict the inner and outer droplets size of the double emulsion. On this basic, we prepare the flame-retardant microcapsules with a dimethyl methylphosphonate (DMMP) inner core and an ultraviolet-curable (UV-curable) polysiloxane shell. It is hopeful that these micro-devices can be employed extensively in the area of microfluidic.

Compliance with ethical standards

Conflict of interest   There are no conflicts to declare.

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