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Development of symmetric and asymmetric straight-through microchannel devices for monodisperse emulsions

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Abstract

Microchannel (MC) emulsification is a promising technique for producing monodisperse emulsions with a coefficient of variation of less than 5% from a microfabricated channel array with a slit-like terrace. We have recently developed an array of deep oblong channels microfabricated vertical to a plate surface as a solution for the low throughput problem of monodisperse emulsion droplets in MC emulsification. This paper presents novel silicon straight-through MC devices for stable and scaled-up production of monodisperse emulsions. The aspect ratio of symmetric oblong channels with a shorter line of about 10 μm and a depth of 200 μm affected considerably the droplet generation behavior. The oblong channels exceeding a threshold aspect ratio of approximately 3 were necessary for producing monodisperse soybean oil-in-water (O/W) emulsions. A large-scale straight-through MC device including about 211,000 oblong channels was successfully used to produce monodisperse O/W emulsions at the maximum droplet productivity of 35 mL/h. We also present a novel asymmetric straight-through MC where an array of asymmetric channels was microfabricated vertical to the plate surface. This asymmetric straight-through MC enabled stably producing monodisperse emulsions using a to-be-dispersed phase of a very low viscosity (e.g. decane) besides soybean oil, overcoming the major drawback of the symmetric oblong channels. The results obtained in this study concluded that stable and scaled-up production of monodisperse emulsions were achieved by scale-up of a straight-through MC device including appropriate oblong channels and development of an asymmetric straight-through MC.

Key words: Straight-through microchannel, Monodisperse emulsion, Symmetric oblong channel, Asymmetric channel, High throughput

1. Introduction

An emulsion is a thermodynamically metastable dispersion of two immiscible liquids that is stabilized by surface active components. Emulsion-based products have been utilized in various fields, including foods, pharmaceuticals, and cosmetics. Droplet size and its distribution of the emulsions greatly affect many important emulsion properties (Orr, 1983; Mason *et al*., 1996; McClements, 2004). Monodisperse emulsions with a typical coefficient of variation "CV, (standard deviation/average droplet diameter, $d_{\mathrm{av}}, \times 100$)" of less than 5% usually have emulsion stability higher than that of polydisperse emulsions. Monodisperse emulsions also can measure, analyze, and control important emulsion properties more clearly than those of polydisperse emulsions (McClements, 2004). However, conventional emulsification instruments such as dispersing machines, colloid mills, and high-pressure homogenizers usually produce polydisperse emulsions (McClements, 2004).

Mason and Bibette (1997) proposed the production of quasi-monodisperse emulsions by shear-rupturing of polydisperse emulsion droplets in an injection couette mixer. Nakashima *et al*. (1991) proposed membrane emulsification for producing quasi-monodisperse emulsions with a CV of approximately 10%. In membrane emulsification, the to-be-dispersed phase is pressed through a microporous membrane to generate size-controlled droplets, while the continuous phase flows across the membrane surface at the low shear stress (Williams *et al*., 1998; Schröder *et al*., 1998; Joscelyne and Trägårdh, 1999; Abrahamse *et al*., 2002). Membrane emulsification using premixed emulsions was effective for the high-throughput production of quasi-monodisperse emulsions (Suzuki *et al*., 1996; Vladisavljević *et al*., 2006). Kawakatsu *et al*. (1997) proposed microchannel (MC) emulsification for procuding monodisperse emulsions from a channel array with a slit-like terrace microfabricated on a silicon plate. The resultant droplet size is primarily controlled by the channel geometry (Kawakatsu *et al*., 2000; Sugiura *et al*., 2002). MC emulsification, with a unique droplet generation mechanism driven by interfacial tension, requires no external shear stress to generate droplets (Sugiura *et al*., 2001). Monodisperse emulsions produced by the preceding techniques have potential food and pharmaceutical applications, including low-calorie fat spread (Katoh *et al*., 1996), multiple drug emulsions (Higashi, *et al*., 1995), microcapsules (Muramatsu and Kondo, 1995; Nakagawa *et al*., 2004), and microparticles (Sugiura *et al*. 2000; Iwamoto *et al*., 2002; Wang *et al*., 2005).

Kobayashi *et al*. (2002) have proposed a straight-through MC device composed of a channel array vertically microfabricated to the plate surface, which is a solution for the low-throughput problem of monodisperse droplets (<0.1 mL/h) in MC emulsification. A straight-through MC with deep, symmetric oblong channels were capable of producing monodisperse emulsions with d_{av} of about 30 μm at a maximum droplet generation rate of 6.5 mL/h (Kobayashi *et al*., 2002). This straight-through MC device has been applied to the production of monodisperse food-grade emulsions (Kobayashi and Nakajima, 2002; Kobayashi *et al*., 2005; Saito *et al*., 2005).

In this paper, we first investigated the effects of the channel aspect ratio and the flow rate of the to-be-dispersed phase on the production characteristics of oil-in-water (O/W) emulsions using straight-through MCs with symmetric oblong channels. We next developed a large scale straight-through MC plate to improve the throughput capacity of monodisperse emulsions. We also propose a novel straight-through MC with asymmetric channels for stable and high-throughghput production of monodisperse emulsions, investigating the production characteristics of O/W emulsions using the asymmetric straight-through MC.

2. Materials and methods

2.1. Straight-through microchannel plate

Figure 1(a) schematically depicts the silicon straight-through MC plate of a standard size with about ten thousands of oblong channels within a 10× 10 mm area in the center of the plate. The plate was microfabricated through photolithography, deep-reactive-ion etching, and thermal oxidization processes (Kobayashi *et al*., 2002). An optical micrograph of the microfabricated oblong channels (Fig. 1(b)) demonstrated that they are of a uniform size. The ratio of the total cross-sectional area of the oblong channels to the total channel area (a 10-mm square) was 4.4% in Fig. 1(b).

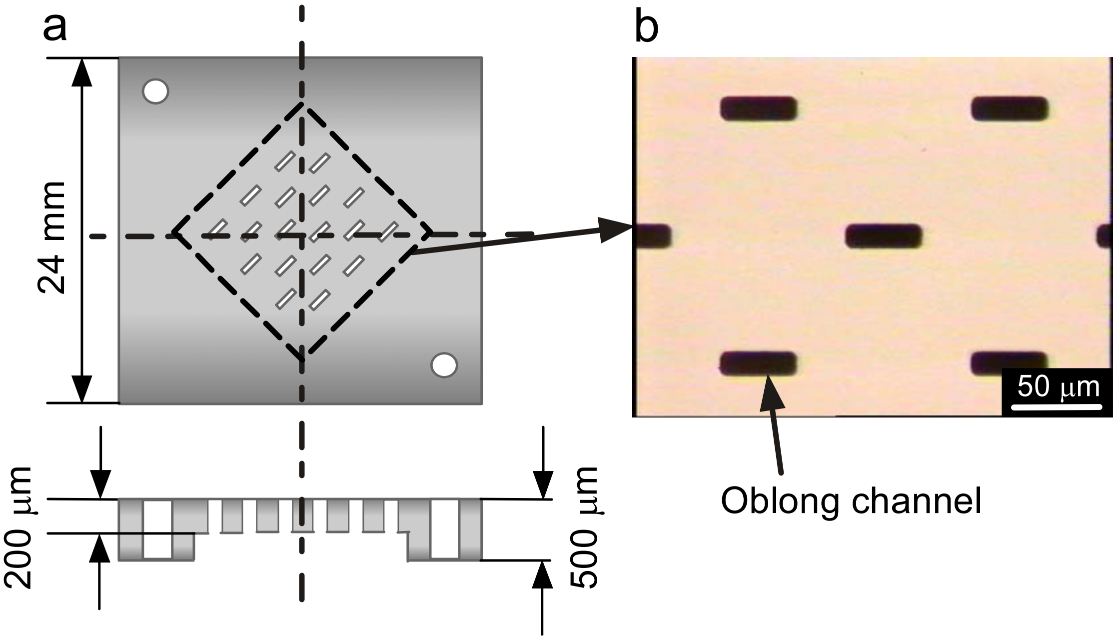

Fig. 1. (a) Schematic of the straight-through MC plate.
(b)Optical micrograph of microfabricated oblong channels.

2.2. Emulsification procedures and analysis

We used refined soybean oil or decane (Wako Pure Chemical Ind.) as the to-be-dispersed oil phase and MilliQ water with 1.0 wt% sodium dodecyl sulfate (SDS, Wako Pure Chemical Ind.) as the continuous water phase. The standard laboratory-scale instrument for straight-through MC emulsification was described previously (Kobayashi et al., 2002). The emulsification module, in which the straight-through MC plate is installed, was initially filled with the continuous phase. The to-be-dispersed phase was supplied into the module by using a syringe pump or by lifting a liquid chamber. The to-be-dispersed phase was then pushed out into the gently moving continuous phase via the channels to generate emulsion droplets, as illustrated in Fig. 2. Droplet generation from the channels was microscopically observed during the experiments (Kobayashi et al., 2002). The average droplet diameter (d_{av}) and CV of the formulated emulsions were determined from 200 droplets in the captured images using WinRoof software (Mitani Co. Ltd.).

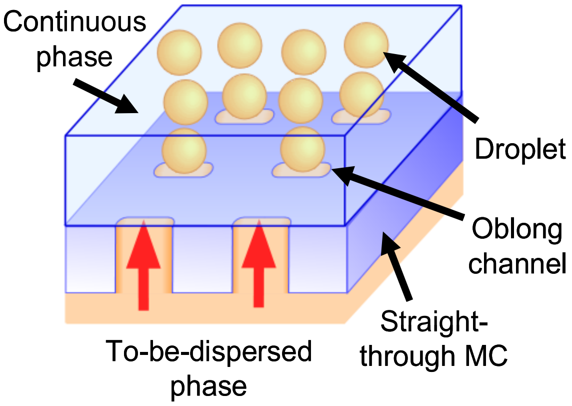

Fig. 2. Schematic of droplet generation from symmetric oblong channels.

3. Results and discussion

3.1. Effect of the aspect ratio of symmetric oblong channels

We used three oblong straight-through MCs with shorter lines of approximately 10 μm and channel aspect ratios of 1.9 to 3.8 (Fig. 3). Straight-through MC emulsification experiments using soybean oil as the oil phase were conducted at an average velocity of the continuous phase along the plate surface (V_c) of 1.2 mm/s, and a flow rate of the to-be-dispersed phase flux (Q_d) of 1.0 mL/h, corresponding to a flux of the to-be-dispersed phase (J_d) of 10 L/(m^2 h). The oil phase that expanded from the channel exit of TMC-1.9 was transformed into polydisperse large droplets with diameters between 350 and 400 μm (Fig. 3(a)). This unstable droplet generation was driven by shear force due to the water-phase flow. The oil phase that expanded from most of active channels in TMC-2.7 was cut off spontaneously into uniformly sized droplets with diameters between 40 and 50 μm, whereas large droplets with diameters over 350 μm were generated from some other active channels (Figs. 3(b) and (d)). As a result, a polydisperse emulsion was obtained using TMC-2.7. When TMC-3.8 was used, all the active channels generated uniformly sized droplets with d_{av} of 41.9 μm and CV of 1.9% (Figs. 3(c) and (e)), demonstrating successful production of a monodisperse emulsion. Our previous paper also reported that the oblong channels with a shorter line of 9.6 μm and an aspect ratio of 3.1 were successfully used to produce monodisperse emulsions (Kobayashi *et al.*, 2002). The results reported in this section revealed that there is a threshold channel aspect ratio over which monodisperse emulsions are successfully formulated for the oblong straight- through MCs with shorter lines of about 10 μm.

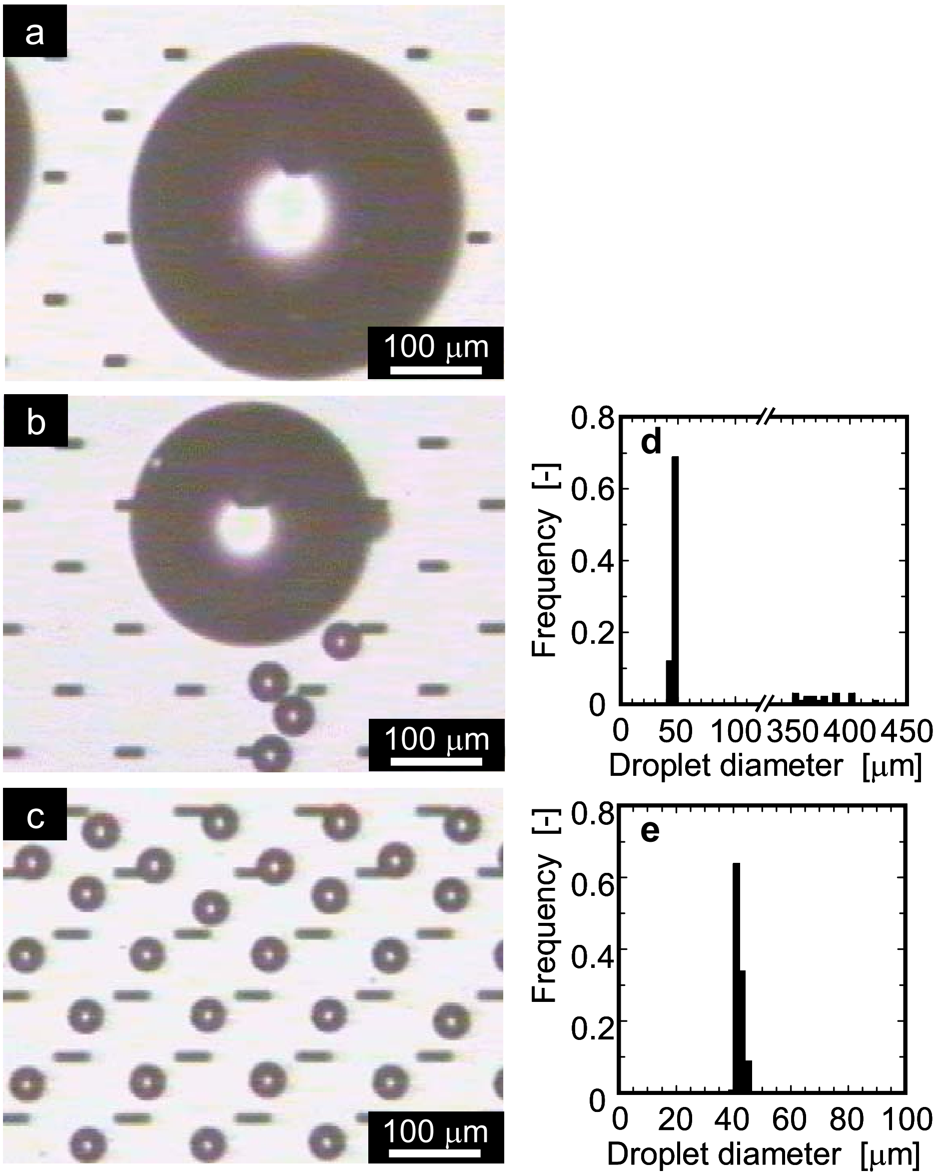

Fig. 3. (a-c) Optical micrographs of droplet generation from symmetric oblong channels. (a) TMC-1.9 with a size of 13.3 × 25.2 × 200 μm (shorter line × longer line × depth), (b) TMC-2.7 with a size of 12.0 × 32.8 × 200 μm, (c) TMC-3.8 with a size of .10.8 × 40.8 × 200 μm.
(d,e) Size distributions of the droplets generated using TMC-2.7 (d) and TMC-3.8 (e).

3.2. Effect of the flow rate of to-be-dispersed phase

The oblong straight-through MC (TMC-5.1) used in this section had a channel size of a shorter line of 9.6 μm, a longer line of 48.7 μm, and a depth of 200 μm. We applied V_c of 1.2 mm/s and Q_d of 1.0 to 10.0 mL/h during the emulsification experiments. Figure 4 shows the effect of Q_d on d_{av} and CV of the produced emulsions. Monodisperse soybean oil-in-water emulsions with d_{av} of about 40 μm and CV of less than 3% were stably produced using the TMC-5.1 at Q_d of 6.0 mL/h or less (Fig. 4(a)). The d_{av} values were independent of the applied Q_d in this region (. The average droplet generation rate of each active channel in the region (a) increased with increasing Q_d and reached six droplets/s. The d_{av} and CV values significantly increased with increasing Q_d between 7.0 and 9.0 mL/h (Fig. 4(b)). Quasi-monodisperse emulsions with CV of 8 to 15% were obtained in the region (b) as an optical micrograph in Fig. 4(b) depicts. The oil phase that expanded from the channel exit was spontaneously cut off into droplets in the regions (a) and (b). A drastic increase in the d_{av} and CV values was observed at Q_d of 10.0 mL/h (Fig. 4(c)); a polydisperse emulsion with large droplets was obtained in the region (c). Steric hindrance among the neighboring oil phase droplets restricted their further expansion and forced them to detach from the channel exit. The oil phase that expanded from the channel exit was no longer cut off spontaneously in the region (c). We thus demonstrated the existence of a critical Q_d value over which the droplet generation behavior and droplet size distribution significantly change in straight-through MC emulsification.

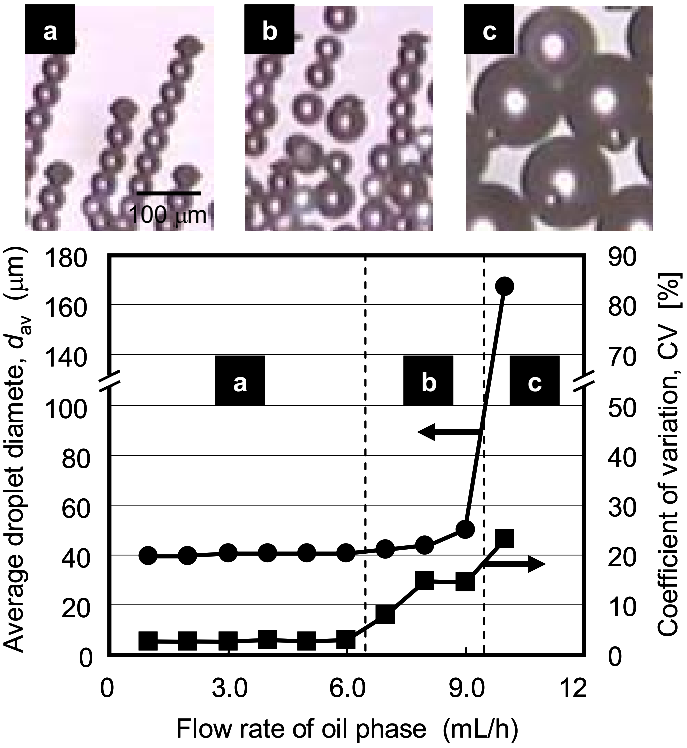

Fig. 4. Effect of Q_d on d_{av} and CV of O/W emulsions produced using TMC5.1.

3.3. Scale up of straight-through MC device with symmetric oblong channels

Figure 5 presents the silicon straight-through MC plate of a large size with about 221,000 oblong channels within four 15 × 15 mm areas in the plate. The oblong channels fabricated in the plate had a channel size of a shorter line of 6.6 μm, a longer line of 26.7 μm, and a depth of 100 μm. The effective channels area of this plate exceeded that of the standard straight-through MC plate (Fig. 1(a)) by about ten times. We applied V_c of 2.2 mm/s and Q_d of 10.0 to 35.0 mL/h during the emulsification experiments. At Q_d of 10.0 mL/h, a monodisperse soybean oil-in-water emulsion with d_{av} of 30.1 μm and CV of 3.9% was stably produced from active channels. Q_d was then increased in steps. Maximum 60% of active channels stably generated monodisperse droplets with d_av of 30.2 μm and CV of 3.3% at Q_d of 35.0 L/(m^2 h), corresponding to J_d of 38.5 L/(m^2 h). In this case, the droplet generation rate per a single device was about 674,000 droplets/s and each active channel generated five droplets per second in average. The above-mentioned results demonstrated that the throughput capacity of monodisperse droplets in a straight-through MC emulsification device was scaled up to several tens of mL/h

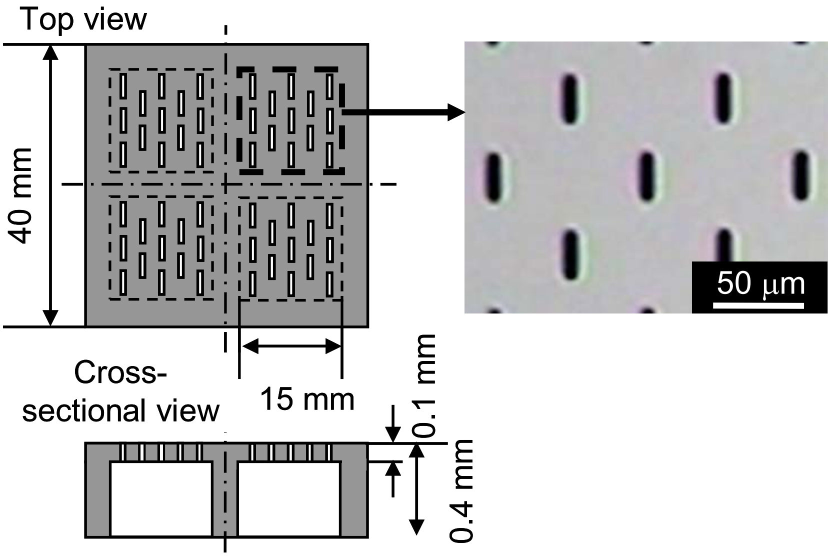

Fig. 5. Schematic of a silicon straight-through MC plate and optical micrograph of symmetric oblong channels.

3.4. Emulsification using an asymmetric straight-through MC

Figure 6 presents an asymmetric straight-through MC consisted of circular channels (9.5 μm in diameter and 5.4 μm in depth) and slits (104 μm in longer line, 11 μm in shorter line, and 21 μm in depth). The SEM micrographs in Figs. 6(b) and (c) confirmed that the slits and channels had highly narrow size distributions.

We examined emulsion droplet generation using the asymmetric straight-through MC. The pressure applied to the oil phase (P_d) was gradually increased during the emulsification experiments. Figures 7(a) and (b) depict examples of droplet generation using the asymmetric straight-through MC. The oil phase that passed through the asymmetric channels expanded into the water phase domain over the plate surface and was spontaneously cut into uniformly sized droplets both for the decane- and soybean oil-containing systems. This result demonstrated that the asymmetric channels overcome the major drawbacks of the symmetric oblong channels: unstable generation of polydisperse large droplets for low viscosity oil-containing systems. The emulsions produced using the asymmetric straight-through MC had d_av and CV of 40.9 μm and 1.3% for decane and of 34.9 μm and 1.9% for soybean oil (Figs. 7(c) and (d)); they are of monodisperse. The ratio of the d_av value to the shorter line of the slit ranged from 3.2 to 3.7, analogous to those in membrane emulsification (Nakashima *et al.*, 1991) and MC emulsification (Kawakatsu *et al.*, 1997). The average droplet generation rate from each active channel reached maximum values of 50 droplet/s for decane and 10 droplets/s for soybean oil. We can explain the advantages of the asymmetric straight-through MC as follows. The circular channel with a minimum cross-sectional area more effectively controls the oil-phase flow in the channel than in the oblong channel because of the greater pressure drop in the circular channel. Moreover, the oil phase that expands in the slit with a distorted, disklike shape can work as a condenser to prevent continuous outflow of the oil phase. We therefore consider that both the slit and circular channel contribute to the stable generation of monodisperse droplets, even using a low viscosity to-be-dispersed phase.

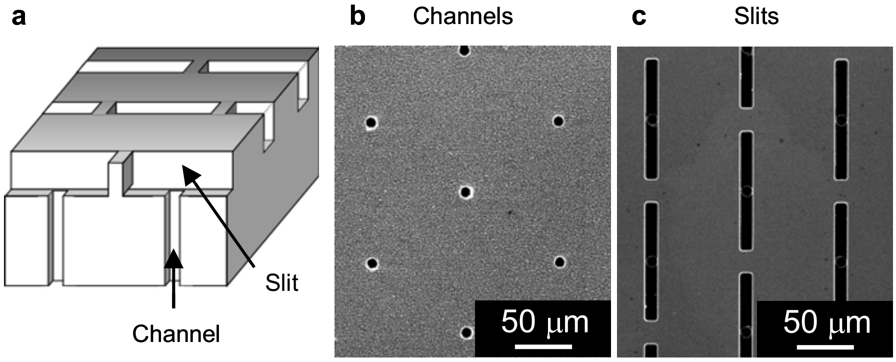

Fig. 6. (a) Schematic of an asymmetric straight-through MC.
(b,c) SEM micrographs of channels and slits.

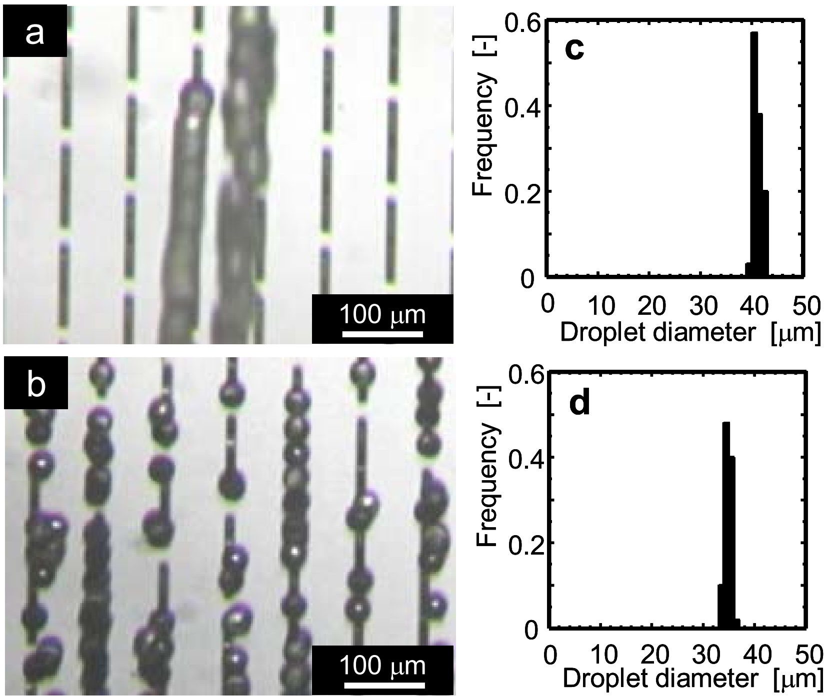

Fig. 7. (a,b) Optical micrographs of generation of O/W emulsion droplets using the asymmetric straight-through MC. (a) Decane, P_d: 2.65 kPa, (b) Soybean oil, P_d: 3.60 kPa.
(c,d) Size distributions of the resultant decane droplets (c) and soybean oil droplets (d).

4. Conclusions

This paper clarified the MC and device structure appropriate for stable production of monodisperse emulsions at high droplet generation rates. Symmetric oblong channels with aspect ratios exceeding the threshold value of about 3 were required for producing monodisperse emulsions. Below the critical Q_d, monodisperse emulsions were successfully produced and their d_av and CV values were independent of the Q_d value. Above the critical Q_d, we observed generation of quasi-monodisperse droplets and of polydisperse large droplets. The throughput capacity of monodisperse droplets in straight-through MC emulsification was scaled up to several tens of mL/h using the large scale straight-through MC plate. The novel asymmetric straight-through MC consisted of slits and circular channels enabled producing monodisperse emulsions, even using a to-be-dispersed phase with a very low viscosity of smaller than 1 mPa s.

Acknowledgement

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