Supporting information

Morphology design and control of polymer particles by regulating droplet flowing mode in microfluidic chips

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Table of Contents

1. Website supplying channel molds S2
2. Manufacture of droplet microfluidic chip S2
3. Comparison of different printing techniques for printing channel mold S4
4. Simple design of channel mould for the manufacture of droplet microfluidic chip S5
5. Simple design of channel mold for the manufacture of droplet microfluidic chip S6
6. Study on shape transition of single emulsion droplets S6
7. Observation of droplet rolling on the inner wall of capillary tube S6
1. **Website supplying channel moulds**
   This company supplied different types of channel molds and the website was shown below. [https://shop111049490.taobao.com/index.htm?spm=2013.1.w5002-7298399646.2.z4ZQja](https://shop111049490.taobao.com/index.htm?spm=2013.1.w5002-7298399646.2.z4ZQja)

2. **Manufacture of droplet microfluidic chip**
   The chip fabrication process is described below. (Fig. S1-S6).
   (1) The chip channel was designed with the CAD software and the channel mold was printed by 3D printer. Any channel shape could be designed easily by the software.

   ![Fig. S1 The designed channel mould by computer assisted software](image1)

   (2) PDMS and curing agent were mixed and poured onto the channel mold in a Petri dish and cured at 60 °C for 2 h (before curing, the PDMS and curing agent were degassed thoroughly for about 20 min). For the solidification of PDMS was free radical initiation, oxygen could inhibit this polymerization process. Thus, excluding oxygen was necessary.

   ![Fig. S2 The demoulded PDMS channel](image2)
(3) After demolding of the PDMS slice on which the channel shape was patterned, it was cut into appropriate square shape based on the microfluidic channels. The holes were punched for the inlets and outlets.

![Diagram](image1)

**Fig. S3** PDMS channel were cut into appropriate shape and inlet/outlet holes were punched.

(4) The capillary tubes were aligned in the channel. A capillary with tapered orifice was injected into another capillary and made sure that the tapered orifices aligned.

![Diagram](image2)

**Fig. S4** Capillary tubes were deposited into the channel.

(5) Epoxy resin was filled in the blanks between capillary tube and square channel.

![Diagram](image3)

**Fig. S5** Epoxy resin was filled in the blanks between capillary tube and square channel.

(6) The PDMS containing capillary tubes was bonded to the glass slide after oxygen plasma treatment.

![Diagram](image4)

**Fig. S6** Glass slide was bonded to the channel slices.
3. Comparison of different printing techniques for printing channel mold

The fused deposition modeling (FDM) technique was compared with stereolithigraphy apparatus (SLA) technique. The precision of FDM and SLA was 0.2 mm and 0.1 mm, respectively. The materials used in FDM and SLA were poly(lactic acid) (PLA) and photo-sensitive resin, respectively. The channel mold printed by FDM shown in Fig. S7B was rougher than the one printed by SLA shown in Fig. S7A. Although the roughness was different, both of them could be used in the preparation of PDMS square channel successfully. It meant that the tiny difference of roughness had no effect on the manufacture of droplet microfluidic chips.

Fig. S7 Comparison of different channel moulds printed by different techniques. (A) Channel mould printed by SLA technique; and (B) channel mould printed by FDM technique.
4. Simple design of channel mould for the manufacture of droplet microfluidic chip

We designed a simple square channel mold and applied for the manufacture of droplet microfluidic chip, as shown in Fig. S8. Fig. S8A - Fig. S8G were the procedures for preparation of droplet microfluidic chips and Fig. S8H was the produced droplet microfluidic chip for single emulsion droplet generation.

Fig. S8 Another type of channel mold for the manufacture of droplet microfluidic chip
5. **Inner structure of double emulsion droplet microfluidic chip**

The detailed structure of double emulsion droplet microfluidic chip was shown below.

![Fig. S9](image)

**Fig. S9** The detailed inner structure of double emulsion droplet microfluidic chip

6. **Study on shape transition of single emulsion droplets**

For the shape transition, the dispersed phase and continuous phase used were red dye doped pure water and 1 wt% Span-80 doped mineral oil, respectively. The velocity of dispersed phase was fixed at 25 μL/h, and the velocity of continuous phase varied from 12.5 μL/h to 800 μL/h.

For the study of shape transition of droplets, the dispersed phase could be changed into FC-40, and the continuous phase could be changed into PFD doped FC-40, ethanol, dimethyl sulfoxide (DMSO), and acetone.

7. **Observation of droplet rolling on the inner wall of capillary tube**

In order to observe the rolling of droplets, we used double emulsion droplet microfluidic chip as a tool. The inner phase was air; the intermediate phase was red dye doped pure water; and the outer phase was 1 wt% Span-80 doped mineral oil. In this system, the air phase was unstable. So the droplets formed containing many tiny bubbles which could be used for the observation of droplet rolling. We fixed the camera head in the side of circular tube for a side view observation. The rolling behavior is shown in Fig. S10 and movie S3.

![Figure S10](image)

**Figure S10.** Rolling of droplets at different time points