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Short communication

Microfluidic devices fabricated using stereolithography for preparation of monodisperse double emulsions

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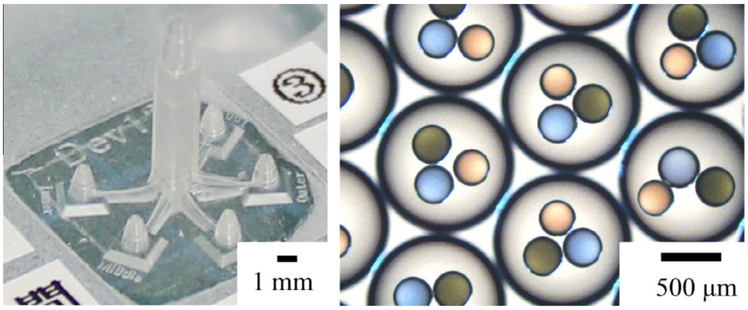
HIGHLIGHTS

- Three-dimensional microfluidic devices were fabricated using stereolithography.
- The devices generate monodisperse O/W/O and W/O/W double emulsions.
- The sizes and numbers of droplets were precisely controlled.
- Monodisperse double emulsions with three different inner droplets were prepared.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate the fabrication of microfluidic devices with three-dimensional flow channels using stereolithography. The fabricated devices can generate monodisperse double emulsions and enable precision control of the sizes and number of encapsulated droplets. In addition, monodisperse double emulsions with three different inner droplets can be generated in a device with three different inner channels. Since devices fabricated using stereolithography can be easily extended to generate higher-order multiple emulsions with more compartments, this method is potentially useful for a broad range of applications in drug delivery, food, cosmetics, and materials science applications.

1. Introduction

Double emulsions are structures consisting of dispersed droplets that contain smaller droplets inside. They can be used as nanoliter reactors and delivery systems for controlled encapsulation and release of active agents in pharmaceuticals, food, cosmetics, and materials science applications [1–7]. For such applications, precise control of the dimensions and structure of the emulsions is crucial because it directly affects the loading levels and release kinetics of the encapsulated substances. Recently, microfluidic devices consisting of networks of flow channels with micrometer dimensions have received increased attention as versatile and powerful tools for preparing double emulsions [8,9]. They can generate a highly monodisperse double emulsion with precision control of the sizes of the inner and outer droplets and number of encapsulated droplets; these cannot be achieved using traditional bulk emulsification methods. To date, several types of microfluidic devices, such as capillary microfluidic devices [10,11] and polydimethylsiloxane (PDMS) devices [12,13], have been developed [14,15]. Capillary microfluidic devices can be fabricated inexpensively by assembling tapered glass capillaries coaxially in a square capillary. The devices offer the distinct capability of creating truly three-dimensional flows, which is critical for various applications, although it is cumbersome to precisely set the positions and sizes of the tapered capillaries. On the other hand, PDMS devices can be

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prepared through the design of mask patterns using the soft lithography technique, which facilitates accurate control of the positions and sizes of channels. However, it is difficult to fabricate a device with complex flow channels in three dimensions; this limits the utility of the device for many applications.

In this communication, we demonstrate the fabrication of three-dimensional microfluidic devices using stereolithography. Stereolithography is a technique that builds a three-dimensional object layer-by-layer through photopolymerization of a liquid monomer resin [16–18]; therefore, it can facilitate the construction of complex flow channels in three dimensions. In addition, since the device is directly fabricated on the basis of computer-aided design (CAD) data on a personal computer without requiring mask patterns, fine-tuning of the channel position and size and redesign can be performed easily and efficiently. We show that three-dimensional devices fabricated using stereolithography can generate monodisperse double emulsions and enable precision control of the sizes and number of encapsulated droplets. In addition, monodisperse double emulsions with three different inner droplets can be generated in a device with three different inner channels.

2. Experimental

We designed a microfluidic device with three-dimensional flow channels for preparing double emulsions using CAD software (SolidWorks), as shown in Fig. 1a. The device has three coaxially aligned cylindrical channels perpendicular to the substrate. The device size was within 1 × 1 cm^2, and the internal diameters of the inner, middle, and outer channels were set to 50, 500, and 1000 µm, respectively. The CAD data was converted into a rapid prototyping format (STL file) and sliced into a set of thin layers. The processing data were then transferred to a stereolithography machine based on a restricted surface method (Sony Corp.), in which a UV laser beam with a wavelength of 365 nm was scanned over a liquid photopolymer epoxy resin (8A54X-9, Sony Chemical & Information Device Corp.) to build the device layer-by-layer on the basis of the sliced data. By adjusting the fabrication conditions, including laser intensity and scanning speed, the desired device could be obtained, as shown in Fig. 1b. The three-dimensional structure was fabricated with an accuracy of less than 5 µm.

In order to prepare double emulsions, the wettability of the flow channels made of the hydrophobic resin must be controlled to generate different wettabilities in different channels [19,20]. For preparation of oil-in-water-in-oil (O/W/O) double emulsions, the wall of the middle channel was coated with hydrophilic silica. A hydrolyzed ethyl silicate solution (N-103X, Colcoat Co.) was injected into the middle channel, and the device was then placed in a 120 °C electric furnace for 30 min to vaporize the solvent and cure the silica coating on the wall [21]. The contact angle of a water droplet on the uncoated surface was 79°, whereas the surface after the silica coating exhibited a hydrophilic contact angle of 33°. Silicone oil (5 cSt, Sigma–Aldrich) and silicone oil (50 cSt, Sigma–Aldrich) containing a surfactant (2 wt.%, RSN-0749, Dow Corning Corporation) were used as inner and outer oil phases, respectively. Ultrapure water containing a red food dye, glycerol (10 wt.%, Wako Pure Chemical Industries Ltd.), and a surfactant (2 wt.%, poly(vinyl alcohol), Mw = 31,000–50,000, Sigma–Aldrich) was used as a middle water phase. They were injected into each channel of the device using positive displacement syringe pumps (Fusion 200, Chemyx Inc.).

3. Results and discussion

Fig. 2a shows the optical micrograph of the formation of monodisperse O/W/O double emulsions in the microfluidic device at flow rates of the inner oil, middle water, and outer oil phases of 0.07, 1.0, and 5.0 mL h^{-1}, respectively. The oil droplet formed at the outlet of the inner channel and was subsequently encapsulated into the water droplet formed at the outlet of the middle channel without loss. The surfactant molecules added to the middle and outer phases immediately migrated to the water–oil interfaces to stabilize the droplets. Therefore, even after collection, the core–shell structure remained stable (Fig. 2b). The obtained O/W/O double emulsions exhibited high monodispersity: The coefficient of variation (CV) values of the sizes of the inner and outer droplets were less than 2%. Similarly, monodisperse water-in-oil-in-water (W/O/W) double emulsions could be obtained in a device with the outer channel coated with a silica layer. Fig. 2c shows the optical micrograph of the prepared W/O/W double emulsions at flow rates of the inner water, middle oil, and outer water phases of 0.06, 3.0, and 20 mL h^{-1}, respectively. The monodisperse water droplets colored with the red dye were encapsulated with monodisperse oil droplets. The CV values of the inner and outer droplets were less than 2%.

One of the most attractive features of microfluidic techniques is the ability to easily and precisely control the sizes of the inner droplets, d_1, and outer droplets, d_2, and number of encapsulated droplets, N_1, of the double emulsions by changing the flow rates of each phase. For example, when the flow rates of the inner and outer oil phases were held at 0.1 and 5.0 mL h^{-1}, respectively, the smaller inner oil droplet was encapsulated with the larger outer water droplet as the flow rate of the middle water phase increased (Fig. 3). The number of the inner droplets, N_1, can be predicted from the inner, middle, and outer fluid flow rates (Q_1, Q_2 and Q_3, respectively) and inner diameters of the middle and outer channels (D_2 and D_3, respectively), from the following equation:

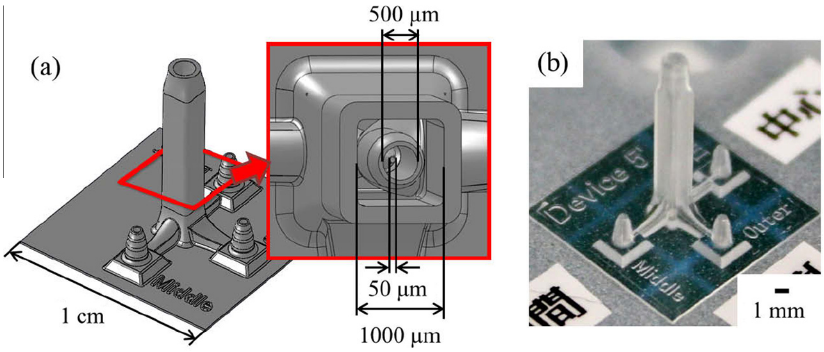

Fig. 1. (a) CAD model of the microfluidic device with three-dimensional flow channels for the preparation of monodisperse double emulsions. (b) Photograph of the microfluidic device fabricated by stereolithography.