

FORMATION OF POLYMER VESICLES UTILIZING PDMS DOUBLE EMULSIFICATION DEVICES

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ABSTRACT

We have successfully demonstrated the formation of polymer microvesicles using 3D-patterned microfluidic devices. Specially-designed PDMS channels are employed to disperse aqueous and polymer solutions into W/O/W double emulsions, which solidify and form microvesicles accordingly. In the prototype demonstration, polystyrene and poly-lactic-acid vesicles are formed through polymerization and solvent extraction, respectively. By varying the outer and inner aqueous-phase flow-rates, the diameter and shell-thickness of the resulting microvesicles could be adjusted almost independently. As such, the presented PDMS emulsification devices could realize the controllability on vesicle formation, which is desired for a variety of applications.

KEYWORDS: Polymer Vesicle, Emulsification, Double Emulsion, Droplet

INTRODUCTION

Because of their great application potential, considerable attention has been attracted to the development of controllable schemes for polymer vesicle fabrication. Recently, researchers have demonstrated double emulsification in various micro-devices utilizing two-step droplet breakup [1, 2] and 3D flow focusing [3, 4]. These devices could have served as great vesicle-forming tools, if neither being limited in applicability nor process compatibility. To address these issues, this paper presents an easy-to-fabricate PDMS device that employs 3D and hydrophilic/phobic-patterned channels to generate double emulsions and corresponding vesicles controllably.

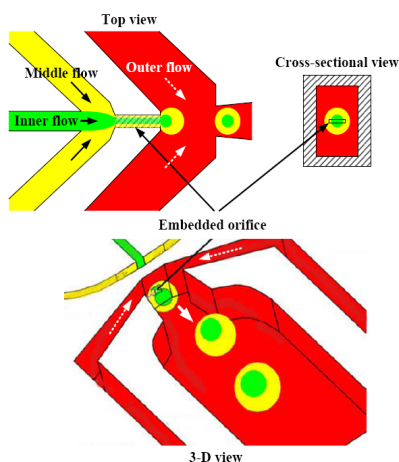


Fig. 1: Schematic of the double emulsification device

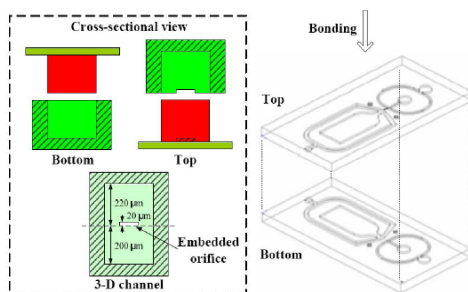


Fig. 2: Fabrication process of the 3D channel

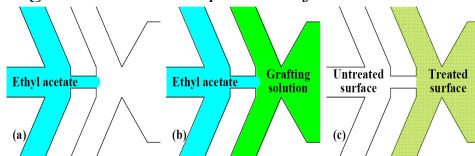


Fig. 3: Selective masking and surface modification process

OPERATING PRINCIPLE

Fig. 1 illustrates the proposed double-emulsification device, which is made up of two adjacent focusing junctions with one embedded orifice connecting in between. First of all, the inner flow is intersected and focused by the middle flow at the upstream junction. While flowing inside the embedded orifice, the inner flow is either shaped into a thread or broken into a series of droplets, depending on the flow rates and viscosities of the fluids involved. Once coming out of the embedded orifice, the W/O coaxial flow is intersected and focused by the outer flow (without touching the downstream channel), and broken into a W/O/W emulsion. It is crucial to include the embedded orifice as part of the 3D focusing mechanism, which could reduce the undesired surface distraction significantly. In the prototype demonstration, two-level SU-8 molds are fabricated to duplicate PDMS microstructures, which are bonded irreversibly to form 3D channels as illustrated in Fig. 2. As shown in Fig. 3, the surfaces of fabricated channels are further patterned with a self-aligned masking process, followed by a photo-grafting reaction [2] that converts the exposed areas into hydrophilic. The grafted surfaces look darker as illustrated in Fig. 4, where a fabricated PDMS device is shown.

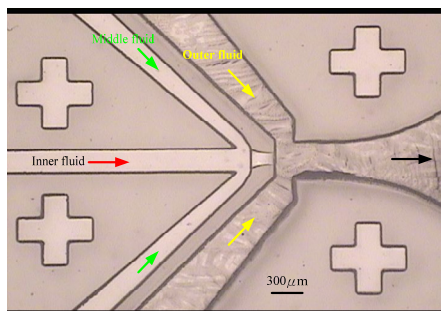


Fig. 4: Photo of a fabricated and surface-modified emulsification device

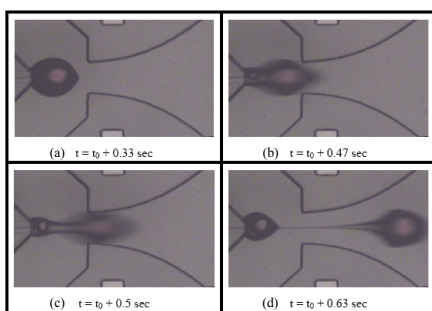


Fig. 5: A captured double emulsification sequence

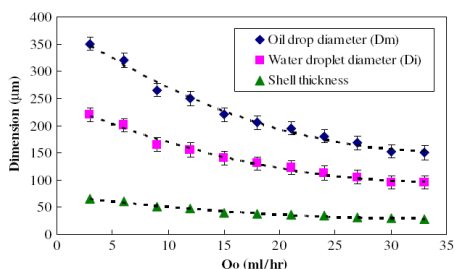


Fig. 6: Relationship between emulsion dimensions and outer fluid flow-rates

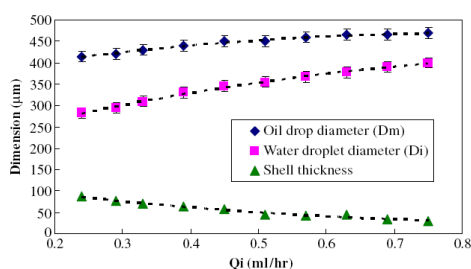


Fig. 7: Relationship between emulsion dimensions and inner fluid flow-rates

RESULTS AND DISCUSSION

Aqueous and polymer solutions are injected into fabricated emulsification devices, while the flow-rates are controlled independently by 3 syringe pumps. In the emulsification trials, dripping is intentionally induced to generate monodisperse

double emulsions with single or multiple droplets inside each polymer-solution drop. Fig. 5 shows a typical double emulsification sequence captured under a microscope. The front of the W/O coaxial flow is (a) held around the exit initially, (b) driven into a convergent channel, (c) accelerated, and (d) finally broken into a drop with just one water droplet inside. It is observed that by varying the flow rates of the three involved fluids, the overall and core diameters of the resulting double emulsions could be adjusted: (1) the overall drop size decreases when the outer fluid flow-rate rises (as shown in Fig. 6), and (2) the shell thickness decreases when the inner fluid flow-rate rises (as shown in Fig. 7). Fig. 8(a) and (b) illustrates two resulting drops with different shell thicknesses. Once the solvent (ethyl acetate) is extracted from the shell or the styrene monomers are polymerized in the shell, the shell solidifies and a polymer microvesicle is formed accordingly as shown in Fig. 8(c).

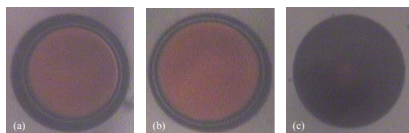


Fig. 8: Photos of resulting emulsion structures and a solidified polymer microvesicle

CONCLUSIONS

This work demonstrates a PDMS emulsification device that is capable of forming polymer microvesicles in a controlled manner. Three accomplishments have been achieved: (1) the design of 3D-patterned PDMS microfluidic devices that can steer and break independently driven aqueous and polymer solution flows into mono-disperse double emulsions; (2) the development of molding, bonding, and selective surface-modification processes that can massively duplicate the microstructures for double emulsification; and (3) the implementation of PDMS vesicle-forming devices that can generate double emulsions and corresponding polymer vesicles with desired structure and size. As such, the presented PDMS emulsification devices could realize the controllability on vesicle formation, which is desired for a variety of applications.

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REFERENCES

- [1] S. Okushima, et al., Controlled production of monodisperse double emulsions by two-step droplet breakup in microfluidic devices, *Langmuir*, 20, 9905 (2004)
- [2] M. Seo, et al., Microfluidic consecutive flow-focusing droplet generators, *Soft Matter*, 3, 986 (2007)
- [3] R. Bocanegra et al., Monodisperse structured multi-vesicle microencapsulation using flow-focusing and controlled disturbance, *Journal of Microencapsulation*, 22, 745 (2005)
- [4] A.S. Utada, et al., Monodisperse double emulsions generated from a micro-capillary device, *Science*, 308, 537 (2005)