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Article

Formation of Polymeric Hollow Microcapsules and Microlenses Using Gas-in-Organic-in-Water Droplets

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Abstract: This paper presents methods for the formation of hollow microcapsules and microlenses using multiphase microdroplets. Microdroplets, which consist of a gas core and an organic phase shell, were generated at a single junction on a silicon device without surface treatment of the fluidic channels. Droplet, core and shell dimensions were controlled by varying the flow rates of each phase. When the organic solvent was released from the organic phase shell, the environmental conditions changed the shape of the solidified polymer shell to either a hollow capsule or a microlens. A uniform solvent release process produced polymeric capsules with nanoliter gas core volumes and a membrane thickness of approximately 3 μm. Alternatively physical rearrangement of the core and shell allowed for the formation of polymeric microlenses. On-demand formation of the polymer lenses in wells and through-holes polydimethylsiloxane (PDMS) structures was achieved. Optical properties of the lenses were controlled by changing the dimension of these structures.

Keywords: multiphase microdroplet; hollow microcapsule; microlens

1. Introduction

With the rapid development of microfluidic and microdroplet technologies, applications for microdroplets have been widely reported in recent years. From biology [1–5] to chemistry [6–9] and medicine [10–13], microdroplets have been used for volume control, protection, and transportation of samples. Moreover, microdroplets have provided an environment for the uniform and functional synthesis of microcapsules in industrial fields such as textiles [14,15] and cosmetics [16]. They have been also used as efficient optical elements for displays [17,18] and detectors [19–21].

Polymeric microcapsules have advanced remarkably using microdroplet technologies. Highly uniform microcapsules have been formed in miniaturized devices, and the functionality of these microcapsules has expanded as a result of new developments in microcapsule synthesis [22–24]. Formation of hollow microcapsules by direct injection of a gas into the capsule core is of particular interest [25–34]. Since the inner cavity and shell layer are formed directly in this technique, the number of materials available for capsule synthesis was significantly increased compared with single emulsion techniques using self-assembly or interfacial polymerization of the shell layer [35–37].

Researchers in this field have typically formed gas cores and shell layers in a T-shaped channel, cross channel, or glass capillary tube. Stone's group used a combination of cross channels and T-shaped channels [25–27]. In this work, core size and shell thickness were independently controlled. However, it was essential to match the generation rate and pitch of the droplets and the method often produced relatively thick shells. In contrast, Luo *et al.* [28–30] and Lee *et al*. [31–33] reported droplet formation methods using three-dimensional glass capillaries. They used a separated serial or simultaneous droplet generation structure to form core and shell layers. However, the fabrication of these glass capillary devices with proper nozzle dimensions also seemed difficult.

In contrast to these methods, we have proposed, in a previous work, a method for generating gas-in-organic-in-water (G/O/W) multiphase droplets on a single-junction silicon device [38]. Gas cores and thin shell membranes were formed with high yield via this simple process. No complicated, difficult fabrication processes were involved to achieve efficient fluidic operation and a reproducible fluidic structure. Using this structure, we developed hollow microcapsules and microlenses from core-shell microdroplets.

The gas core and organic shell droplets can be changed into a Janus droplet [39,40] according to its environmental condition such as stirring, thus our process has the flexibility of altering the positioning and arrangement of the droplets by varying synthesis conditions. In our method, the density of the gas core and the organic shell materials differed greatly. Therefore, when we varied the stirring and solidification conditions for the G/O/W droplets, organic shell layers were transformed into either a hollow capsule or a bowl-like or lens-like shape [41]. Lens-shaped structures can be potentially used in optical element production. Since the volume of gas core and the properties of the organic shell dictate the lens shape, optical properties of these lenses can be controlled by varying the fluidic conditions.

Based on this new technology, we developed a prototype on-demand microlens production system in wells and through-holes on wells and through-holes.

Hence, the polymeric materials and formation methods derived from our gas core and polymeric shell droplet technology can be useful for various applications in materials science and chemistry.

2. Formation of Hollow Microcapsules and Microlenses

We prepared microcapsules and microlenses based on our previous work on gas-in-organic-in-water (G/O/W) microdroplets [38]. As shown in Figure 1a, the gas was directly injected into the core of the organic shell layer, like blowing up a balloon. This simultaneous formation of a core and shell at a single junction allowed us to prepare a more stable and reliable multiphase droplet. This technique also provided for increased yield. Since our microcapsule polymers are soluble in the organic shell layer, we could produce specific polymeric structures by controlled release of organic solvent.

The shape of the polymer shell depends on the conditions of the solidification process. In the case of G/O/W droplets, the density of the gas core and organic shell was lower than that of water, so the droplets floated on the water surface. The organic layer was thus in contact with both water and atmospheric air and the organic solvent could be released into both. Hence, control of the shape of the polymer layer was possible by controlling the stirring conditions. When the stirring and release conditions were uniform, we obtained hollow microcapsules with a uniform polymeric shell, as shown in Figure 1b(i). In contrast, when there was not externally applied force, the gas core and organic shell rearranged according to their density. Consequently, lens-like organic layers formed with a spherical gas core, as shown in Figure 1b(ii).

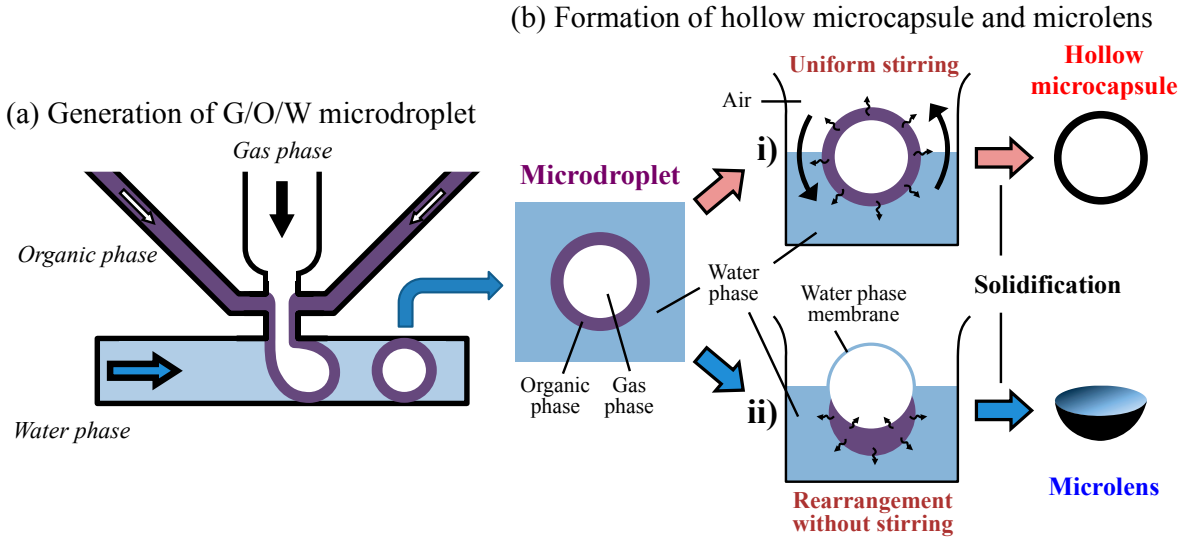

Figure 1. Steps in the formation of microcapsules and microlenses using gas-in-organic-in-water (G/O/W) microdroplets. (**a**) Generation of G/O/W microdroplet; (**b**) formation of hollow microcapsule and microlens.

3. Device Design and Fabrication

The device used for microdroplet generation consisted of a multiphase junction, an observation area, three inlets, one outlet, and various microchannels, as shown in Figure 2. The three inlets were

designed to channel the gas, organic phase and water, respectively, onto a single junction. Microdroplets generated were observed within a cylindrical area 1 mm in diameter (the size of the droplets was larger than the width of the water phase channel).

A two-step photoresist pattering and silicon etching process formed the fluidic channels. The three inlets and one outlet were formed by etching the backside of a 200 μm thick silicon wafer to a depth of 100 μm using a deep reactive ion etching (DRIE) process. A second DRIE process was then applied to the front side of the silicon wafer. This second etching step produced the multiphase junction, observation area, and channels. The etching depth on the front side was also 100 μm. This procedure formed all of the channels for microdroplet generation and the through-holes for inlets and outlets, and also protected the fragile, fine patterns from contamination and mechanical damage during the second DRIE and cleaning process. Then we anodically bonded the front side of the newly pattered silicon wafer to glass (TEMPAX Float, Schott, Mainz, Germany) for visualization and fluidic sealing. Finally, we bonded copper ports to the backside for connection of the inlet and outlet tubes for use in our fluidic experiments.

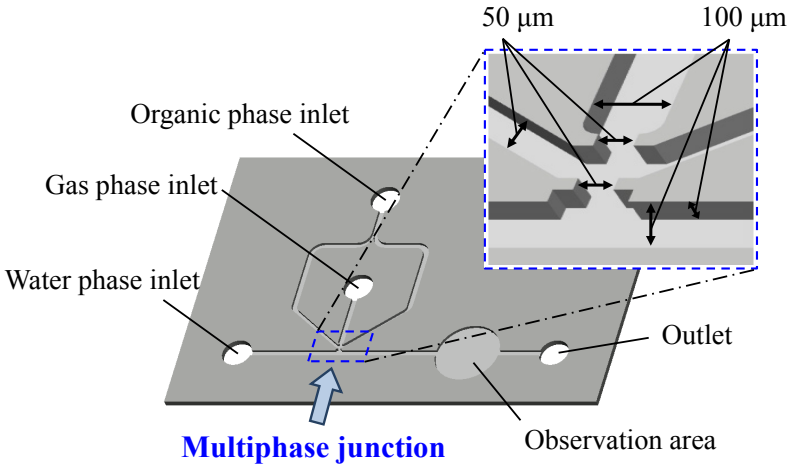

Figure 2. Silicon wafer design for microdroplet generation and, in the inset, detail of the multiphase junction.

4. Results and Discussion

Fluids used to form the G/O/W droplet were as follows: The gas phase was air, the organic phase was a solution of 5 wt % polystyrene (MW: 250000) in dichloromethane, and the water phase was a solution of 3 wt % polyvinyl alcohol (PVA) in deionized water. Polystyrene was selected because it is a widely available plastic with excellent manufacturability and hardness. Dichloromethane was selected because it is a good polystyrene solvent that has solubility in water and a high rate of evaporation in air. Furthermore, we used the PVA solution as a dispersion agent solution to prevent the generated droplets from merging with one another.

A syringe (1750CX, Hamilton, Reno, NV, USA) and syringe pump (KDS210, KD Scientific, Holliston, MA, USA) were used to inject the water and organic phases into the channels. A pressure regulator (2657 pneumatic pressure standard, Yokogawa, Tokyo, Japan) controlled the gas phase pressure. A high-speed camera (FASTCAM-NEO, Photron, Tokyo, Japan) monitored the continuous generation of droplets. Droplet size was measured by pixel analysis of the captured images.

4.1. Generation of G/O/W Microdroplets

As shown in Figure 3, microdroplets were successfully generated at a multiphase junction. Gas was directly injected into the organic membrane via the vertical channel, and then the gas and fluid phases were inflated which formed the G/O/W droplets.

The flow rates of each of the three phase fluids determined the gas core size and the organic membrane thickness of the droplets. Figure 4 shows the dimensions of the G/O/W droplets *versus* the flow rates of each fluid phase. Gas core size increased linearly with an increase in gas pressure, as shown in Figure 4a. Gas core size decreased linearly with an increase in the organic phase flow rate, as shown in Figure 4b. The size of whole droplets did not change dramatically relative to the size of the gas core when the gas pressure and organic phase flow rates were changed. We expected that, under a fixed water phase flow rate, droplet size would increase when the sample flow rate in the common T-junction increased, but this did not occur. The droplet consisting of organic and gas phases showed different results with W/O and O/W droplet generation. We believe this is because the gas and organic solution have different physical properties, surface tensions and viscosities. Consequently, the two fluids' different properties and hydrodynamic shear force in the T-junction resulted in the different droplet sizes, hence, the minimum size of the generated droplets shifted up and down based upon the specific conditions of these two phases.

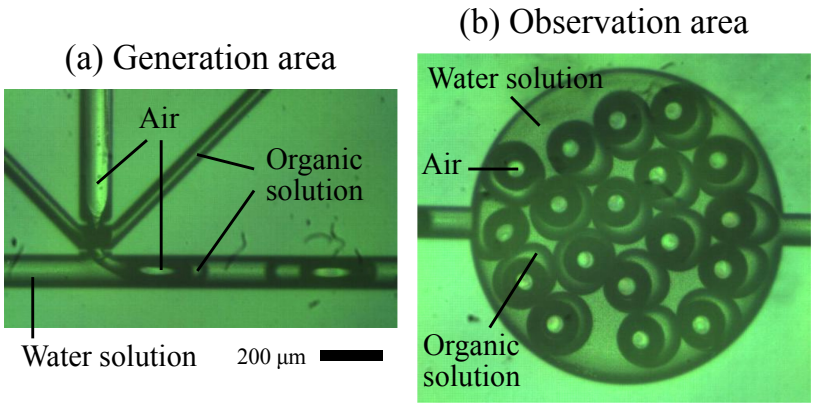

Figure 3. Images of G/O/W microdroplets in (**a**) the generation area within the multiphase junction and (**b**) the observation area.

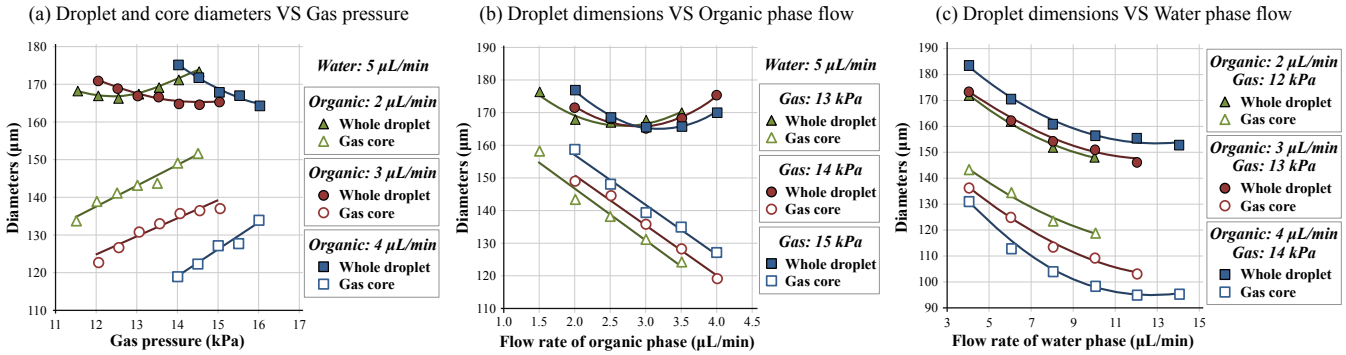

Figure 4. Results of the multiphase droplet generation that occurred by controlling the flow rate of each phase fluid. (**a**) Droplet and core diameters *vs*. gas pressure; (**b**) droplet dimensions *vs*. organic phase flow; (**c**) droplet dimensions *vs*. water phase flow.

In contrast, the droplet and gas core size decreased simultaneously when the water phase flow rate increased, as shown in Figure 4c. Furthermore, the droplet and core size changed when the organic flow rate and gas pressure was changed.

In conclusion, we demonstrated the systematic and independent control of droplet size, gas core size, and organic membrane thickness of microcapsules by varying the flow conditions of each fluid phase. We generated diameters of the droplet and gas core diameters ranging from 184–147 μm, and 159–95 μm, respectively.

4.2. Formation of Microcapsules

Microdroplets were solidified into microcapsules in a 1% PVA distilled water solution while stirring of 200 rpm using magnetic stirrer so that uniform release of the organic solvent could occur. As shown in Figure 5, microcapsules were successfully generated using this process. Before solidification, the diameter of the droplet was about 160 μm. After the solidification process was completed, the diameter of the microcapsules ranged from 145 to 165 μm. Compared to single phase droplet solidification, shrinkage was minimal due to the presence of the gas core, but the gas volume tended to change due to the surrounding pressure and temperature.

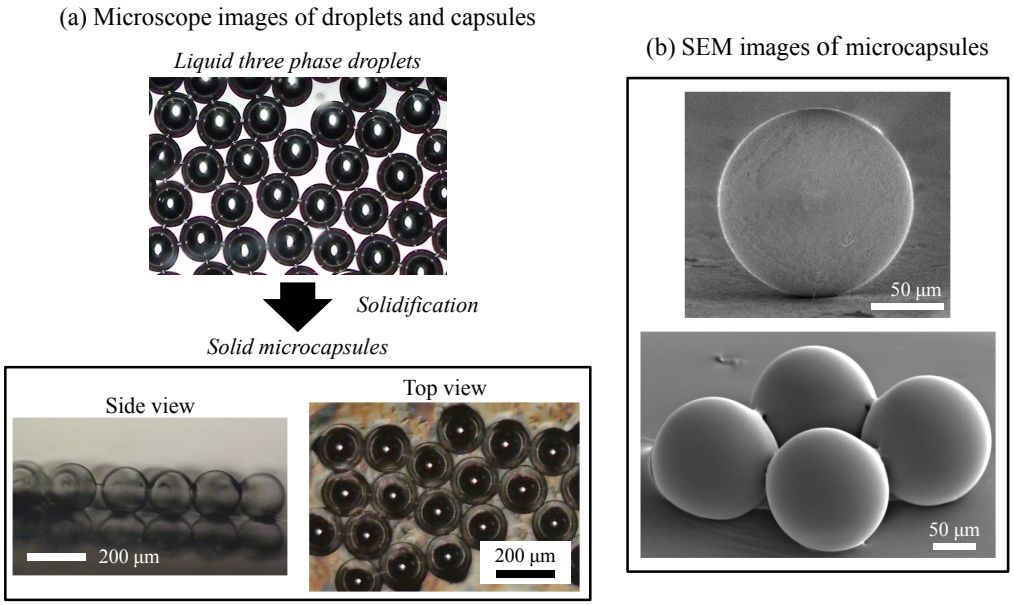

Figure 5. Images of solidified microcapsules.

FIB (focused ion beam) lithography was used to measure the dimensions of the inner cavity and thickness of the polymer shell. The results of the partially etched polystyrene hollow capsules are shown in Figure 6. Applied voltage was 40 kV, current was 0.29 nA, and etching time was 60 min. Thickness of the membrane was approximately 3 μm, and the layer formed as a solid polymer without any holes or pores. Furthermore, their inner cavities were clearly observed.

Some deformed capsules were observed as shown in Figure 7. We believe these defects occurred because of changes in pressure and temperature as the thin membrane covering the inner gas core sealed itself over time. We interpret the presence of partially damaged thin shell membranes (Figure 7a) as evidence that the sealing of the inner gas core did indeed occur over time. Torn and

deformed microcapsules by external force (Figure 7b) showed the thin shell membrane and inner cavity again. In addition, the capsule shell was sufficiently thin and fragile to be melted by excessive electric power applied for metal coating on the capsule surface, as shown in Figure 7c.

We showed that our stirring and solidification process allowed different shapes, such as bowl-like or lens-like polymer structures to form, as well as hollow microcapsules, as shown in Figure 8. These different shapes occurred independently of the conditions of the droplet's formation. More detailed studies of how varying conditions influence microcapsule formation is under investigation.

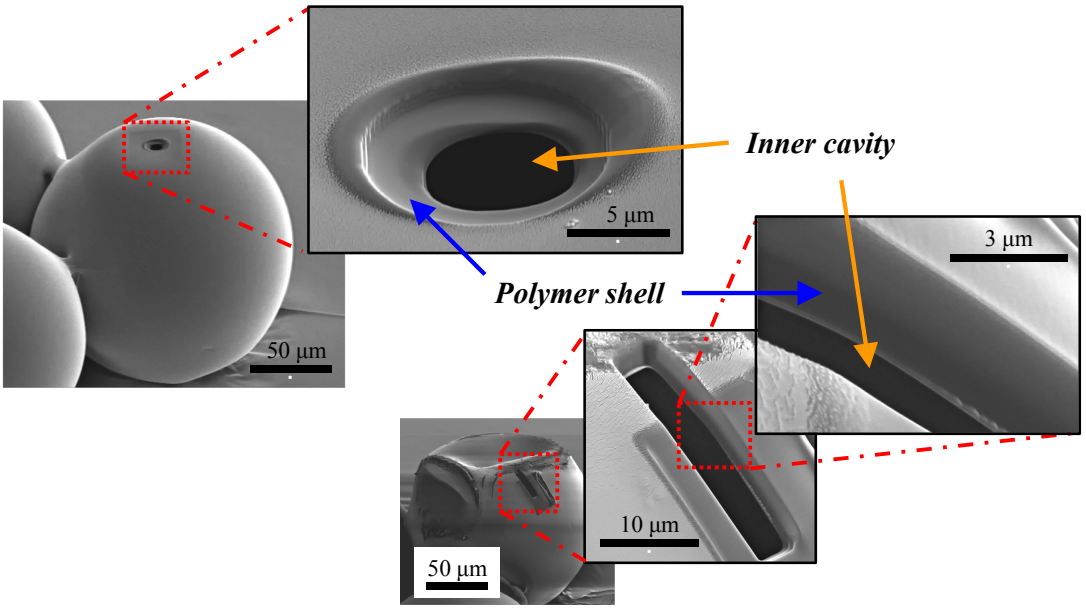

Figure 6. Partially etched microcapsules using focused ion beam (FIB) lithography showing shell membranes and inner cavities.

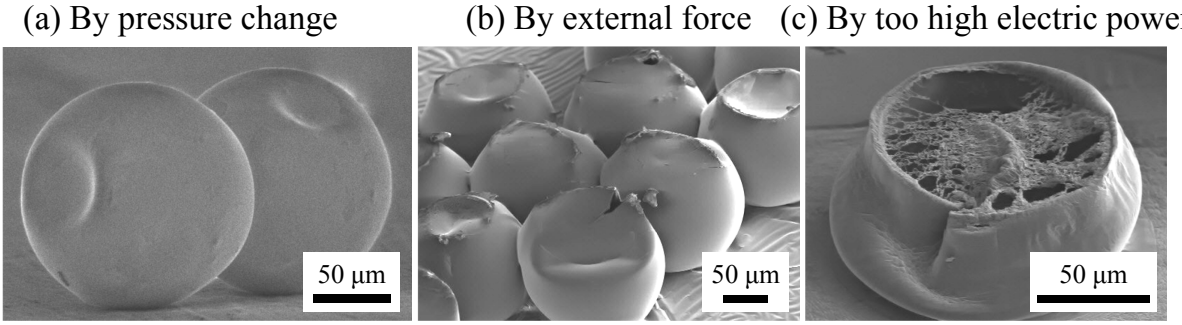

Figure 7. Images of deformed capsules: (**a**) By pressure change; (**b**) by external force; (**c**) by too high electric power.

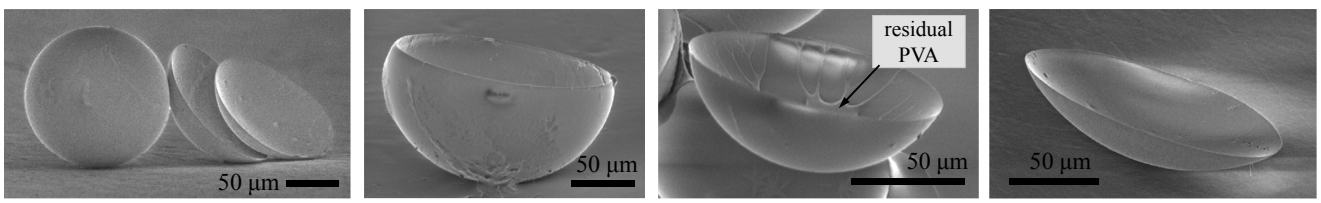

Figure 8. Various shapes of capsules, bowl-like and lens-like, resulting from different solidification conditions.

4.3. Formation of Microlenses

We used the work discussed above to form a microlens at a specific position on a PDMS (polydimethylsiloxane) structure. The gas-included droplet has a lower density than the surrounding aqueous liquid, so the G/O/W droplet floated. If there were structures such as a well or a through-hole above the initial position of the droplets in water, then the droplets would enter into the structure. If no external treatment such as stirring was used, the relatively heavy organic phase rearranged and formed a lens-like shape under the gas core (Figure 9a).

In Figure 9b, we show G/O/W droplets of about 190 μm in diameter placed on a PDMS well structure. A polymeric lens formed after rearrangement and solidification of the organic layer. We could control the size and curvature of the lens by changing the dimensions of the well structure. We were able to produce well sizes from 100 to 150 μm, lens radii from 128 to 166 μm, and radii of curvature from 88 to 120 μm. Radius and radius of curvature of the microlens were large by an increase in droplet volume. We were also able to form high-density lens arrays on PDMS through-holes.

Optical properties of the polymer lenses formed on different well structures were evaluated. We were able to focus a microlens formed within a PDMS well on an image of "JPN" printed on paper and view the result using a microscope (see Figure 10). The lens shape was changed by altering the well dimensions, so we could change magnification and focal distance by the different lens dimensions. These results told us that we could control the optical properties of the lenses by altering the dimensions of the structures in which droplets are placed, as well as altering the dimensions of droplets that form microlenses.

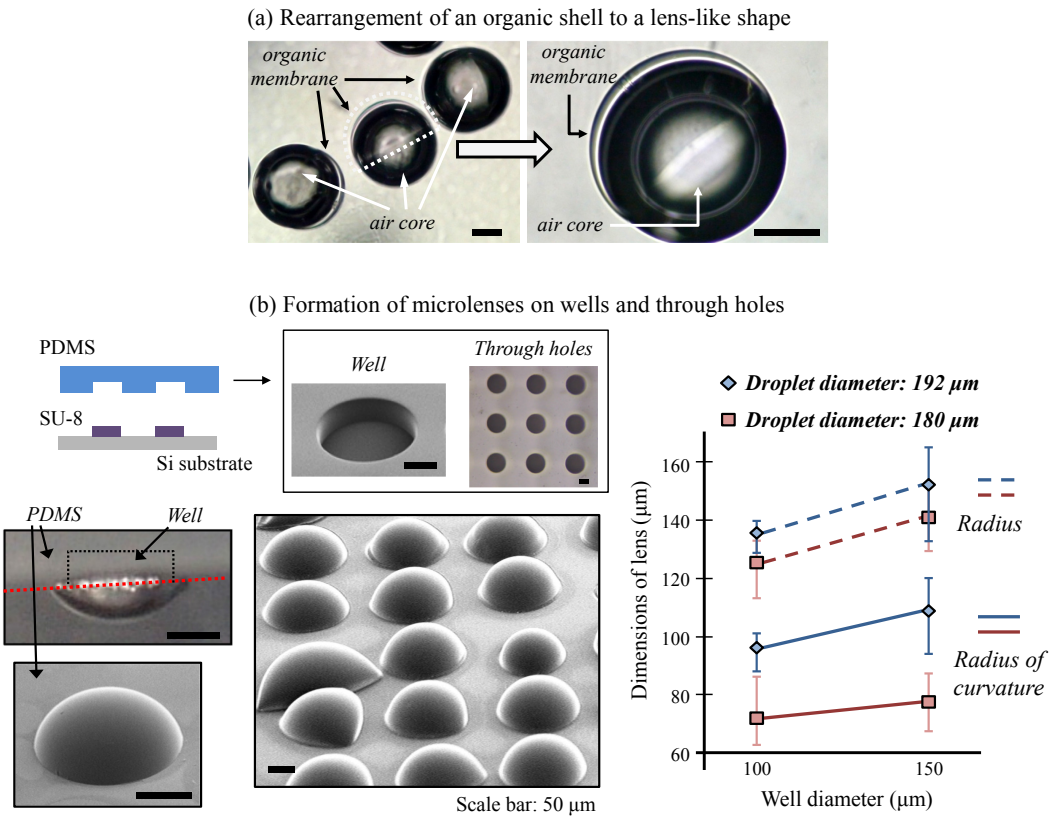

Figure 9. (**a**) Rearrangement of organic shell layers; (**b**) on-demand microlens formation on a polydimethylsiloxane (PDMS) structure.

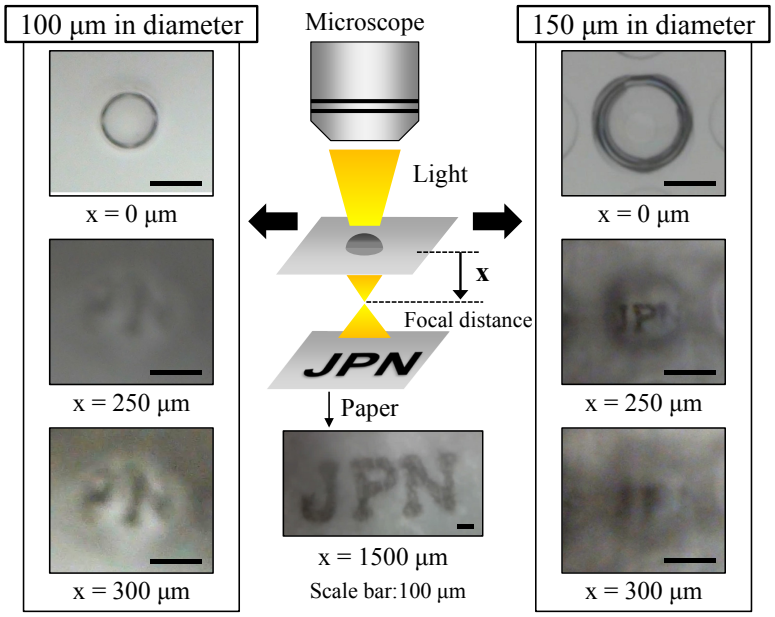

Figure 10. Optical microscope images of different microlenses formed by the same droplets but on different wells.

4.4. Discussion

Compared to liquid droplet generation, the solidification process for microcapsule and microlens formation required particular conditions. Our work showed that capsule and lens formation and the shape of the solidified polymer were strongly dependent upon release conditions of organic solvent. We also demonstrated that the environmental conditions of the microcapsule/microlens system during its formation affected the gas core volume and the shell membrane thickness. Change in temperature also caused partial deformation of sphere capsules.

In addition, we determined that the efficiency of lens formation using a through-hole array was higher than using a well array. When we used a well array, the lens-like polymer layer frequently fell of the PDMS structure because this structure did not allow gas in the core to escape and large volumes disrupted contact of this structure with the polymer. Even using the through-hole structure, however, careful handling was required to assure microdroplets actually form microlenses.

5. Conclusions

The polymeric hollow microcapsules and microlenses were successfully formed using gas-in-organic-in-water microdroplets. We controlled the size of the microdroplets and gas core by adjusting the flow rates of the gas, organic, and water phases. We could form microdroplets in hollow microcapsules or microlenses depending upon the solidification conditions employed. Hollow microcapsules formed when we used uniform stirring conditions. A non-porous polymer shell was formed with a membrane thickness of 2% of the capsule diameter, which effectively sealed the gas core for long periods of time. Furthermore, microlenses were formed from the core and shell materials that had greatly different densities. Under some conditions, microlenses formed on both well and through-hole structures. We could adjust the size and optical properties of the microlenses by adjusting the size of the PDMS structures.

The multiphase microdroplets were formed by a simply modified T-junction structure without surface treatment. This work provided practical applications of the multiphase microdroplets and potential availabilities to a variety of materials and synthesis methods. We believe our microcapsule device and synthesis methods will have a wide range of application in chemistry and biology. In addition, we believe our lens formation methods using multiphase droplets will have applications in the formation of in-channel and on-demand optical components.

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Author Contributions

Dong Hyun Yoon, Takahiro Arakawa and Shuichi Shoji conceived and designed the device and experiments; Dong Hyun Yoon and Kenta Hasegawa fabricated devices and performed the experiments; Yuji Kaneko partially fabricated the device; Dong Hyun Yoon, Jeung Sang Go, Tetsushi Sekiguchi and Shuichi Shoji contributed materials and analysis; Dong Hyun Yoon wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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