Trapping and collection of uniform size droplets for nanoparticle synthesis

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This paper presents a simple and fast method for droplet trapping and collection and demonstrates nanoparticle synthesis inside these trapped droplets. Since droplet trapping is size-dependent, droplets having various sizes caused by unstable inlet flows can be eliminated. Moreover, the new droplet substitutes the previous one, so we can keep the up-to-date contents of droplets at all times. All trapped droplets can be simply collected at the outlet. We had demonstrated the synthesis of iron oxide nanoparticles inside droplets and collection of them from the device. Due to its simplicity and high efficiency for selective trapping and collection, this method can become one of the key essentials in droplet-based microfluidic assays.

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Integrated droplet-based microfluidic systems have been a powerful tool for biological and chemical applications. Digital microfluidic operation provides a perfect isolation of each droplet from the surrounding environment. High throughput generation of micro-droplets also makes it possible for massive reaction and analysis at the same time. In droplet-based assays, droplets flow inside a microchannel at a high speed, which is effective for rapid reaction and analysis. However, there are many assays where reactions are not fast enough, and each droplet should be monitored or immobilized for further detection and analysis. In chemical reactions such as nanoparticle synthesis, aqueous solutions containing nanoparticle precursors should be remained and continuously mixed at temperature zones for nucleation and growth in order to obtain monodisperse nanoparticles. At the end of the synthesis, droplets need to be retrieved for the collection of nanoparticles.

There are several methods proposed for droplet trapping and collection based on various kinds of actuation principles. Hydrodynamic force exerted from inlet pressure can push droplets into trapping structures and maintain them inside. Trapped droplets are collected at the inlet by supplying reverse flow from the outlet. However, the carrier fluid should be supplied continuously in order to keep droplets inside. Any small fluctuation of flow or vibration from the external environment causes droplets to elude from the trapping structures. Other methods utilizing optical, dielectrophoretic, and acoustic actuations also require external power and control, thus increase the cost and complexity. In some of these methods, only a few droplets are manipulated one at a time, which reduces the throughput dramatically.

In this paper, we introduce a simple and fast method for droplet trapping and collection using surface tension of droplets. Droplet trapping is size-dependent; therefore, droplets having various sizes caused by unstable inlet flows can be eliminated. Every new coming droplet substitutes the previous one; this keeps fresh and stabilized droplets in the wells at all times. There is no need for any additional controls for selective trapping of droplets, and all trapped droplets can be simply collected at the outlet by increasing the flow rate of the carrier fluid.

When a droplet has a diameter larger than a microchannel, it becomes compressed to a thickness less than its spherical diameter. As a droplet enters a well, which is large enough to restore its spherical shape (Fig. 1), the droplet is trapped at the well and cannot exit easily due to surface tension. If the droplet diameter is smaller than the depth of the microchannel, it maintains its spherical shape and it does not get trapped. Also, droplets with diameters larger than the depth of the well cannot be trapped because their portion outside of the well is dragged by the viscous force and removes itself from the well. Therefore, only droplets compressed in the microchannel with diameters similar to the width of the wells are trapped and remained.

The droplet inside the well can exit by the substitution of the next incoming droplet. Viscous force caused from high flow of the carrier fluid can also release droplets from the wells. Droplet substitution by incoming new droplets can be useful, especially when there is a chemical reaction inside.

FIG. 1. (Color online) Nanoparticle synthesis using selective droplet trap in a well array. Satellite droplets smaller than a well diameter are not trapped and dragged by viscous force: (a) side view; (b) top view.

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the droplet, because we can maintain up-to-date contents of droplets all the time. Since flow rates at the beginning are not stable, analytic contents inside the droplet, usually made from the mixture of two or more aqueous solutions, are inadequate for analysis. From our method, these droplets can be substituted by adequate ones, and this is effective to synthesize mono-disperse nanoparticles inside droplets. Once the flows stabilize, the droplets can be kept in the wells by stopping aqueous fluid flows. For the collection of all trapped droplets, we simply increase the flow rate of the carrier fluid; thus, high viscous drag force will bring all droplets to the outlet of the chip.

The height of the microchannel and wells are 50 and 100 µm, respectively. Wells are designed to have a cylindrical geometry having the same diameter as target droplets, 200 µm. The width of the microchannel is 600 µm, and wells are 100 µm apart from both side walls. There are 512 wells in a chip, and size of the chip is 28 mm × 23 mm (Fig. 3(a)). To predict the droplet behavior near the designed well, numerical estimation using COMSOL Multiphysics was conducted, as shown in Fig. 2. Simulations show that once the droplet is adjacent to the well, it enters the well within 1 ms and returns to its spherical shape due to surface tension. This result supports our observations in our experiments.

Devices were fabricated in polydimethylsiloxane (PDMS) by the soft lithography technique. The master mold was made out of SU8-3050 and was patterned by using UV photolithography. Before the development of the unexposed SU8 layer, another layer of SU8 was coated on top of it. After patterning the well array on top of the microchannel, both SU8 layers were developed together. PDMS mixture of base and cross linker (10:1, wt.) was poured on the SU8 mold and cured. After peeling off the PDMS layer from the mold, the inlet and outlet holes on PDMS layer were punched and bonded to a glass slide after oxygen plasma treatment.

In the experimental study, hexadecane with 2% (wt.) surfactant (Span 80) was used as the continuous phase while deionized water was used as the discrete phase. Both water and hexadecane were supplied to the chip independently by a two-headed syringe pump. Hexadecane was injected first to fill up the entire channel and wells. The air bubbles trapped in wells were diminished after several minutes of hexadecane injection, and then, water was injected. Flow rates of continuous and discrete phases were 1000 and 200 µl/h, respectively. Until a stabilized flow was maintained in the channel, droplets of various sizes were generated due to unstable flow in the microchannel. Droplets with comparable sizes to the wells were only trapped as they encountered an empty well. In the meanwhile, small and large droplets passed the well array without being trapped. After droplet size stabilization, new incoming droplets substituted droplets in pre-occupied wells continuously as described earlier. Figure 3(b) shows successive trapping and substitution of a droplet in a well. Once droplet generation is stabilized and all droplets are replaced, droplet generation and trapping can be stopped by simply stopping the aqueous solution injection while hexadecane flow continues. As the pressure in syringes and tubing decreased, the size of generated droplets decreased, and small droplets began to pass wells without being trapped or substituted. Among the 512 wells in the chip, 508 wells contained a single droplet with trapping efficiency of 99.2%. All trapped droplets were collected at the outlet as oil flow rate increased up to 4000 µl/h. The size of droplets trapped in wells was uniform.

In order to show the capability of the device for chemical synthesis we demonstrated iron oxide nanoparticle

FIG. 2. (Color online) Numerical estimation of droplet behavior in a well.

FIG. 3. (Color online) The present chip: (a) overall view with a large view of channel and well array with designed dimensions; (b) droplet trap and substitution in a well. Each time frame between images was 1/30 s.
synthesis. Nanoparticles are formed by hydrolyzing an aqueous solution containing 1.5 mmol FeCl$_3$·6H$_2$O and 1 mmol FeCl$_2$·4H$_2$O (reagent 1) with a 2M aqueous NH$_3$OH solution (reagent 2) following the method in Ref. 4. Reagents enter the device from separate channels, briefly mix, and form a droplet in a third channel where hexadecane is the carrier fluid (Fig. 4(a)). Nanoparticles are generated as reagents mix inside the droplet (Fig. 4(b)). The density of nanoparticles inside initial droplets was high due to the unstabilized flow of aqueous solutions, but decreased as the flow saturated, and these initial droplets were substituted by the stabilized new ones. Post-processing was done by centrifuging the solution obtained after the synthesis inside an ethanol and acetone mix in order to remove the hexadecane. After three times of repeated centrifuge, particles are imaged by Transmission Electron Microscope (TEM). The synthesized particles are shown in Fig. 5.

In summary, we presented a simple method for trapping droplets by their size and collecting them. The synthesis of nanoparticles inside droplets was successfully demonstrated in the fabricated chip. Due to its simplicity and high efficiency for selective trapping and collection, this method can become one of the key essentials in droplet-based microfluidic assays.

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