연성 미세유체 소자를 이용한 콜로이드 집합체 설계

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Colloidal Assembly Designed on Soft Microfluidic Chips

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서론

Monodisperse spherical colloids such as polymer latexes and silica suspensions serve as model systems for practical colloidal materials or biological systems because of their uniform response to external electromagnetic and flow fields.[1] Recently, various organic or inorganic monodisperse colloidal dispersions with non-spherical shapes such as ellipsoids, dumbbells, and hollow spheres have been demonstrated.[2-5] Their complexity may make it possible to fabricate novel photonic band gap materials as well as to model real colloids with more irregular structures. Colloidal superstructures from monodisperse particles have been proposed as alternative way to novel model colloid or better building blocks for PBG materials. For example, two-dimensional (2D) colloidal aggregates with well-defined size, shape and structure were obtained under 2D confinement in a patterned photoresist film and simple heterogeneous colloidal aggregates were prepared using specific chemical or biochemical interaction between two kinds of monodisperse colloids.[6-9] Recently, 3D homogeneous colloidal assemblies with well-defined structure and shape have been reported.[10-11] However, it is still challenging to fabricate 3D colloidal assemblies designed at micrometer length scales. In this presentation, we demonstrate soft-lithography-based microfluidic chips as designing tools for the fabrication of micron-sized uniform 3D colloidal assemblies of monodisperse latex. Our strategy is first to generate a monodisperse particle-containing water-in-oil emulsions in soft microfluidic devices (see Figure 1a) and then produce uniform spherical colloidal assemblies by slowly removing the water from the droplets. While standard cross-flow techniques have generated monodisperse emulsion by forcing the discontinuous phase into an open continuous phase through narrow pores,[12] microfluidic chips are more versatile tools for generation of the monodisperse emulsions or vesicles because droplet generation process is easy to be visualized and designed by controlling the surface properties and laying out flow channels.[13]

실험

The soft microfluidic chips in our experimentals are fabricated by pouring silicone prepolymer(polydimethylsiloxane; Sylgard184, DowCorning) on a silicon wafer mold containg positive-relief channels patterned in thick photoresist(AZ9260, Clariant), which is then cured at 80°C, for 40 min. Then, the replicated channels in PDMS are completely enclosed with a coverslip coated with precured thin layer of PDMS through an additional curing at same temperature, for 1.5 hours. The measured channel dimensions are approximately 60 ㎛ wide × 7 ㎛ high, tapering to 15 ㎛ × 6 ㎛ in the region where the water and oil meet at the crossflow intersection (Figure 1). The fluids are introduced into the PDMS microfluidic devices through pressurized reservoirs containing suspension and oil. Pressure was applied to the reservoirs with compressed nitrogen, and the device output channel was allowed to vent to the atmosphere.

결과 및 토론

In soft microfluidic chips mounted on optical microscopy, uniform emulsions have been generated at regular intervals by classical droplet break-off processes at the junction of two microfluidic channels as shown in Figure 1(b,c). Balance of surface tension and high shear forces at the leading edge of the water perpendicular to the oil flow determine the diameter of picoliter-scale droplets and generation frequency. Because the system remains at low Reynolds number, generated droplets are moving in pattern as they are formed. As in Thorsen's previous work, segregated droplet pattern was created under conditions where the water pressure is lower than the oil pressure (see B, C, and H pattern in Fig. 3 of Ref. 12). Generated droplets suspended in oil have kept moving along the microchannel and was shrunk down slowly as water was dissolved in oil phase (Figure 2a). Finally, consolidated spherical colloidal assemblies were obtained at end of microchannel (Figure 2b).

PDMS is not compatible with all kinds of oils. Specifically, low molecular hydrocarbon oil is lethal to PDMS microfluidic devices. According to our test, Silicone and Fluorine-modified oil were suitable oil appropriate for our PDMS, which were purchased from Gelest and ShinEtsu, respectively. Additional conditions for our experimentation are that they should dissolve water slightly for obtaining the particle assemblies finally and colloidal latex particles should be stay in droplets without escape from droplet. In our previous work, we found that above two kinds of oil satisfied these requirement for our study while other system like mixture of mineral oil and surfactant cause the particles in aqueous phase to escape oil phase and then encapsulated droplets were destroyed spontaneously. Therefore, we did not used sufactnat in oil phase, which also facilitated the shrinkage of droplet diameter. However, water soluble surfactant as stabilizer of latex particles inside was added for preventing particles from adsorbing to PDMS channel wall for there was no repulsion force between PDMS channel wall and particle, which was prepared by emulsifier-free emulsion polymerization.

As shown in Figure 2b, we produced uniform colloidal assemblies at micrometer scale. However, statistical variation of particle number is more critical as total number of particle inside is going down (see Figure 3). Particle number density is very important in developing novel photonic crystals using colloidal assemblies as building units. We could figure out the exact number of particle inside from two dimensional planes shown in video movie file. While there is small number fluctuation around a few percentages for large number of particle, number fluctuation of colloidal aggregate with small number of particle is so critical that we couldn't tell that those generated colloidal assemblies were not uniform. Therefore, if uniform colloidal assemblies for photonic crystals, other following process might be required including dielectrophoretic separation, sorting devices, and so forth. Despite of these disadvantage, most of colloidal assemblies with relatively large number of particle inside are still interesting other application such as model colloids for complex colloidal particles, paper-like display and nanobarcode for recognition of biological molecules.

Figure 3 show the typical examples of colloidal crystallite from our soft-lithography-based microfluidic devices. Colloidal assemblies could be modeled as schematic diagram shown in left side, which might contain about fifteen colloidal particles in Figure 3a and four colloidal particles in Figure 3b. Although all kind of the colloidal assemblies were not identified, these pictures shows that suspension droplets could be crystallized into defect-free colloidal assembly inside droplets if the right number of particles were encapsulated at droplet generation step.

정리

In summary, we have established that soft-lithography-based microfluidics and droplet break-off dynamics can be combined to produce uniform colloidal assemblies from monodisperse suspension emulsions. Experimental results described here have shown that fairly uniform colloidal assemblies were prepared within statistical error due to particle number fluctuation. We believe that this approach could be extended to small colloidal assemblies by using more complicated soft-microfluidic devices, which have been already developed by one of our research group. As well, other microfluidic channel design or different microfluidic chip made out of more chemically inert materials could be applied to similar experiment to get lots of interesting colloidal assemblies including non-aqueous suspension droplet, complex colloidal assemblies of multi-sized colloidal particles.

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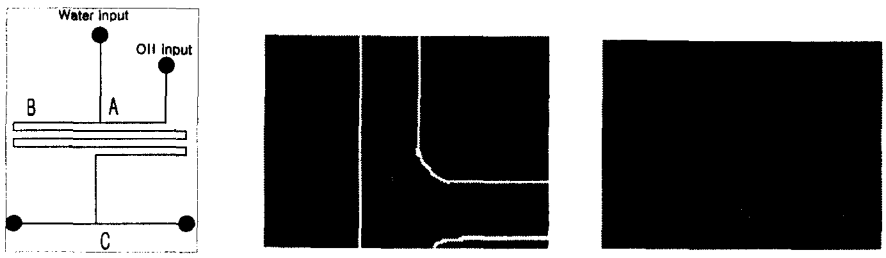
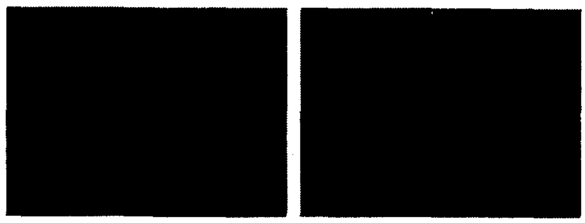


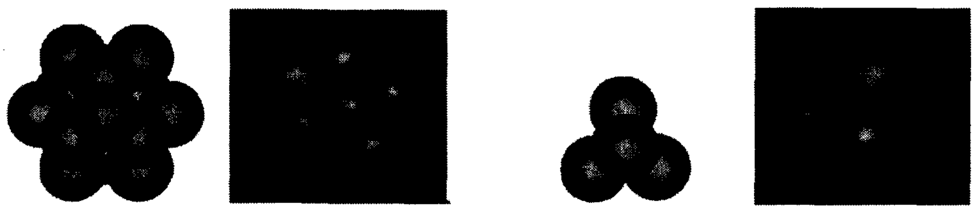
(a) (b) (c)

Figure 1. Layout of microchannel (a) and optical micrographs of uniform emulsion generation. (b,c)



(a) (b)

Figure 2. Droplet shrinkage during the traveling of suspension droplet along the microchannel (a) and consolidated colloidal assemblies (b) (inset shows the tetrahedra colloidal assembly)



(a) (b)

Figure 3. Model and optical micrographs of colloidal assemblies, which contain fifteen (a) and four beads (b) are shown in left and right, respectively.