

Generation of uniform photonic balls by template-assisted colloidal crystallization

Gi-Ra Yi^a, Seog-Jin Jeon^a, Todd Thorsen^b, Vinothan N. Manoharan^c,
Stephan R. Quake^d, David J. Pine^{c,e}, Seung-Man Yang^{a,*}

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea

^b Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^c Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA

^d Department of Applied Physics, California Institute of Technology, Pasadena, CA 91125, USA

^e Department of Materials, University of California, Santa Barbara, CA 93106, USA

Abstract

Uniform assemblies of all-identical colloidal particles, so-called *photonic balls*, are produced by injecting an aqueous suspension of polymer latex spheres into a surfactant-laden oil phase at an oil/water junction of capillary tubes or soft-microfluidic devices. The size of these assemblies can be controlled by varying the injection pressure or particle concentration.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Monodisperse emulsions; Colloidal crystals; Photonic crystals; Soft-microfluidics

1. Introduction

Three-dimensional (3D) assemblies of sub-micrometer monodisperse colloids have received much attention recently, primarily because of their potential uses as photonic crystals [1,2]. Face-centered cubic colloidal crystals, formed spontaneously in all-identical spherical colloids, such as polymer latexes or silica suspensions, are the simplest examples of such assemblies. More complex structures can be made by a variety of clever techniques, such as altering the shape of the colloidal particles [3–6], directing their assembly with patterned surfaces [7,8], or tuning the interactions between particles [9–11]. Recently, spherical colloidal assemblies of controlled shape and size have attracted a great deal of interest because regularly shaped particles are useful in a variety of applications, such as size-exclusion chromatography (separation), catalysis, and absorption. Furthermore, these assemblies, if their size could be down to micrometer scale, may serve as building blocks for more complex colloidal assemblies, including, perhaps, new types of photonic crystals. More importantly, these may be used to develop highly efficient scatterers that could be used as light diffusers in a wide variety of applications. Henceforth, these well-defined structured materials will be referred to as

“photonic balls” because of their unique photonic properties resulting from the arrangement of colloids with spherical shape. Although similar spherical assemblies have been prepared [12–14], the preparation of small (micrometer scale) and monodisperse aggregates is still challenging. In this paper, we will mainly describe the experimental detail of making such uniform photonic balls using micropipettes or soft-microfluidic devices and show some pertinent results.

2. Experimental

Our photonic balls are micrometer-sized 3D colloidal assemblies with narrow size distribution and an ordered internal structure consisting of monodisperse latex particles. They are prepared by either generating a monodisperse water-in-oil emulsion using a droplet break-off technique developed by Umbanhowar et al. [15] or using emulsion-generating soft-microfluidic devices of Thorsen et al. [16], where the water (droplet) phase of our emulsions contains polymer particles. Finally, uniform spherical colloidal assemblies were produced by slowly removing the water from the aqueous suspension droplets.

2.1. Micropipette injection

As shown in Fig. 1, an aqueous suspension of monodisperse polymer beads is injected into an ambient fluid through

* Corresponding author. Tel.: +82-42-869-3922; fax: +82-42-869-3910.
E-mail address: smyang@mail.kaist.ac.kr (S.-M. Yang).

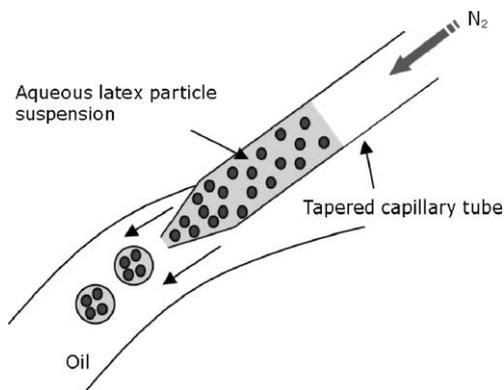


Fig. 1. Schematic diagram for generation of monodisperse suspension emulsion using micropipettes.

a tapered capillary tube (a micropipette) with inner diameter of either 5 or 10 μm . A 7 cm diameter transparent plastic cup with surfactant-laden oil phase was rotated at a constant speed. When a constant angular velocity of the cup was achieved and surface fluctuations disappeared, the end of a micropipette (World Precision Instrument, μ -Tip) was immersed in the continuous oil phase. Uniform emulsions were generated by pressure-driven flow through the immersed tip. For suspension emulsions, particle aggregates or dust, which could cause clogging, were removed by filtering the suspension with a 0.8 μm membrane (Millipore, Millex-AA). Mineral oil (heavy) and fluorinated silicone oil (henceforth FSO; FMS-123) were purchased from Fisher Scientific and Gelest, respectively.

Sub-micrometer polystyrene spheres with hydrophilic surfaces were used for the aqueous latex suspension, which were synthesized through emulsifier-free emulsion polymerization of styrene with hydrophilic comonomers by following the literature [17]. Poly(styrene/acrylamide) particles possessed a mean diameter of 450 nm, as measured by using a dynamic light scattering system (Brookhaven Instruments Inc.), while poly(styrene/styrene sulfonate) particles had a mean diameter of 235 nm. Both the latexes had polydispersities of 5% or less. Comonomers were used to make the surfaces of the particles hydrophilic, which prevented clogging the micropipette tips.

2.2. Soft-microfluidic approach

In soft-microfluidic devices, uniform emulsions were generated at regular intervals by droplet break-off at the junction of two microfluidic channels as shown in Fig. 2a. Generated droplets suspended in oil kept moving along the microchannel and was shrunk down slowly as water was dissolved into the oil phase. Finally, consolidated spherical colloidal aggregates were obtained at the downstream of the microchannel.

The microfluidic devices utilized in our experiment were fabricated by pouring polydimethylsiloxane (PDMS; Sylgard 184, DowCorning) on a silicon wafer mold containing positive-relief channels patterned in a photoresist (AZ9260,

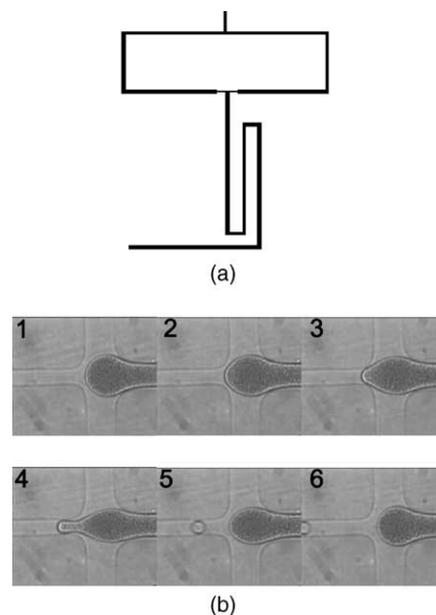


Fig. 2. (a) Schematic diagram of T-type microchannel design for monodisperse suspension emulsion generation. (b) Optical micrographs of monodisperse emulsion generation containing 0.235 μm beads at T-type junction of suspension and silicone oil (ShinEtsu, $\nu = 100 \text{ cSt}$) phase.

Clariant), which was then cured at 80 $^{\circ}\text{C}$, for 40 min. The channels were fully encapsulated by curing the patterned PDMS on a coverslip coated with a thin layer of PDMS and by bonding the two layers together through an additional curing at the same temperature, for 1.5 h. The measured channel dimensions were approximately 60 μm wide \times 10 μm high, tapering to 35 μm \times 8 μm in the region where the water and oil merged at the T-type intersection (Fig. 2). The fluids were introduced into the PDMS microfluidic devices through pressurized reservoirs containing the aqueous suspension and the oil. The reservoirs were connected to the device through approximately 30 cm long Tygon tube of 500 μm i.d. Pressure was applied to the reservoirs and regulated by compressed nitrogen, and the device output channel was allowed to vent to atmosphere. All reported pressures were in the gauge scale (psig). FSO (FMS-123, Gelest) and silicone oil (KF-96, ShinEtsu) with kinematic viscosity of 500 and 100 cSt, respectively, were used. The silicone oils were compatible with elastomeric silicone microfluidic devices and absorbed water slightly.

The latex particles were stabilized by electrostatic interaction between the particles, which were prepared by emulsifier-free emulsion polymerization. However, the latex particles were likely to adsorb onto the PDMS channel wall, which could cause the channel clogging. To prevent the particle adsorption onto the PDMS channel wall, water soluble surfactant was added to the aqueous suspension phase. We tested several polymeric surfactants, including Tween 20 (Aldrich), hydrophilic methyl methacrylate graft copolymer (Atlox 4913, UniQema), and triblock copolymer (Pluronic P123, BASF).

3. Results and discussion

Using both the experimental systems of micropipette injection and microfluidic devices, we have successfully prepared monodisperse emulsion continuously, which has entailed spherical colloidal crystals of micrometer size through evaporation-assisted colloidal crystallization.

3.1. Micropipette injection

To prepare the monodisperse suspension emulsion, we injected 1.1% (w/w) aqueous latex spheres into mineral oil containing 2.0% Span 80. Although we were able to obtain monodisperse emulsions in the early stage, after several hours we observed that the particles had escaped the droplets. The instability was due to the fact that the surfactant diffused into the droplets and adsorbed onto the polymer spheres, rendering them hydrophobic. As the instability was a result of the affinity of the polymeric particle being stronger for the oil phase than for the aqueous phase, there were two approaches to remedy the problem: the first was to increase the hydrophilicity of the polymer particles by increasing the amount of hydrophilic comonomer, while the second was to reduce the polymer–oil affinity. Since we were not sure about the mechanism of surfactant adsorbing onto the particles, we chose the second approach here. Instead of the mineral oil, we used FSO as the continuous phase and a custom surfactant as stabilizing agent for the water-in-FSO emulsion, which was a diblock copolymer of fluorinated silicone and polyethylene glycol, synthesized as described in [18]. Fig. 3a shows the photonic balls that were produced from monodisperse aqueous suspension emulsions containing poly(styrene/acrylamide) particles of 450 nm in diameter at 1.1% (w/w). These emulsions were produced using a 5 μm micropipette at a constant rotational speed of 55 cm/s under 2.0 psig. Initially, the mean diameter was about 16.7 μm , and the particles inside the droplet moved around randomly due to Brownian forces. However, as the water was removed into the continuous phase (water is slightly soluble in FSO), the droplets shrank until, after 12 h, we obtained about consolidated colloidal assembly of 4 μm in diameter (see inset of Fig. 3a). We could control the size of the assemblies by changing the synthesis conditions, the suspension concentration, or particle diameter. Fig. 3b shows well-ordered 6.3 μm photonic balls made from 230 nm poly(styrene/styrene sulfonate) particles and their image under the optical microscopy is reproduced in Fig. 3c.

3.2. Soft-microfluidic approach

Microfluidic devices are versatile tools for generation of the uniform emulsions because droplet generation process is easy to be visualized and changed by designing the microfluidic channel. Balance of surface tension and high shear forces at the leading edge of the water that is perpendicular to the emerging oil flow determine the diameter of

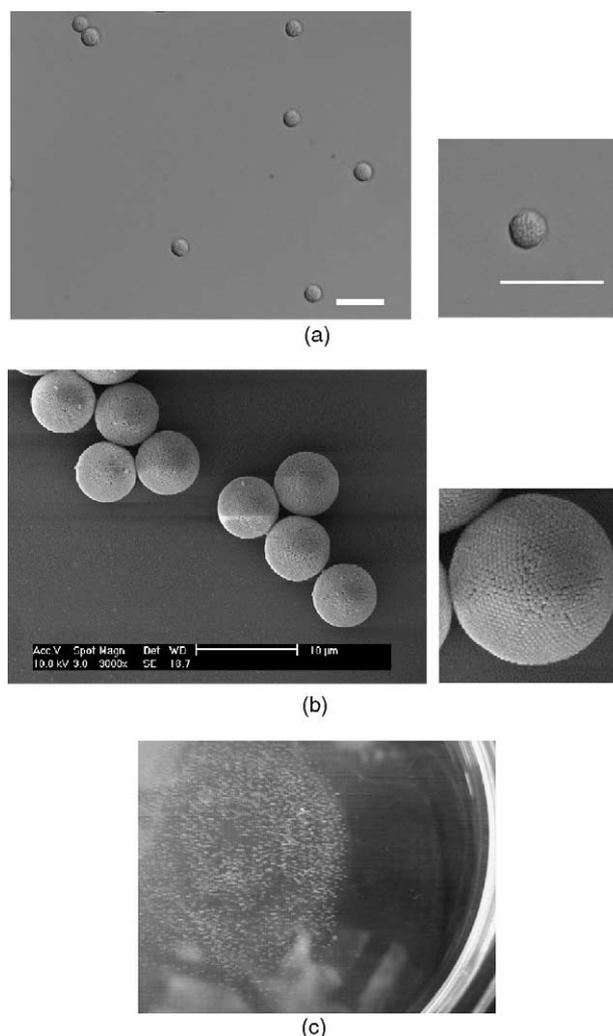


Fig. 3. (a) Optical micrographs of spherical colloidal assemblies after consolidation from suspension droplets in FSO (generation conditions: 1.1% (w/w) suspension; $d_{ii} = 5 \mu\text{m}$; $u = 55 \text{ cm/s}$; $P = 2.0 \text{ psig}$). Scale bars: (a) 10 μm ; (inset of (a)) 4 μm . (b) Scanning electron micrograph of colloidal assemblies obtained from a 2.0% (w/w) suspension of 230 nm poly(styrene/styrene sulfonate) particles ($d_{ii} = 10 \mu\text{m}$; $u = 53 \text{ cm/s}$; $P = 1.0 \text{ psig}$); and (c) their photographic image.

picoliter-scale droplets and generation frequency. Because the system remains at low Reynolds numbers, generated droplets are moving in a pattern as they are formed. As in the previous work of Thorsen et al., in which various dynamic pattern formations of emulsions were investigated by modifying the relative pressures of water and oil, segregated droplet pattern was generated under condition where the water pressure was lower than the oil pressure (e.g. B, C and H patterns in Fig. 3 of [16]). The viscosity of oil phase and channel width or shape influenced the size of droplets. As the viscosity of oil increased, droplet diameter decreased at a given pressure difference. The channel width at T-type junction also affected the size of droplets. It is noteworthy that no stabilizer was needed in the oil phase because the generated droplets did not run into each other in our linear

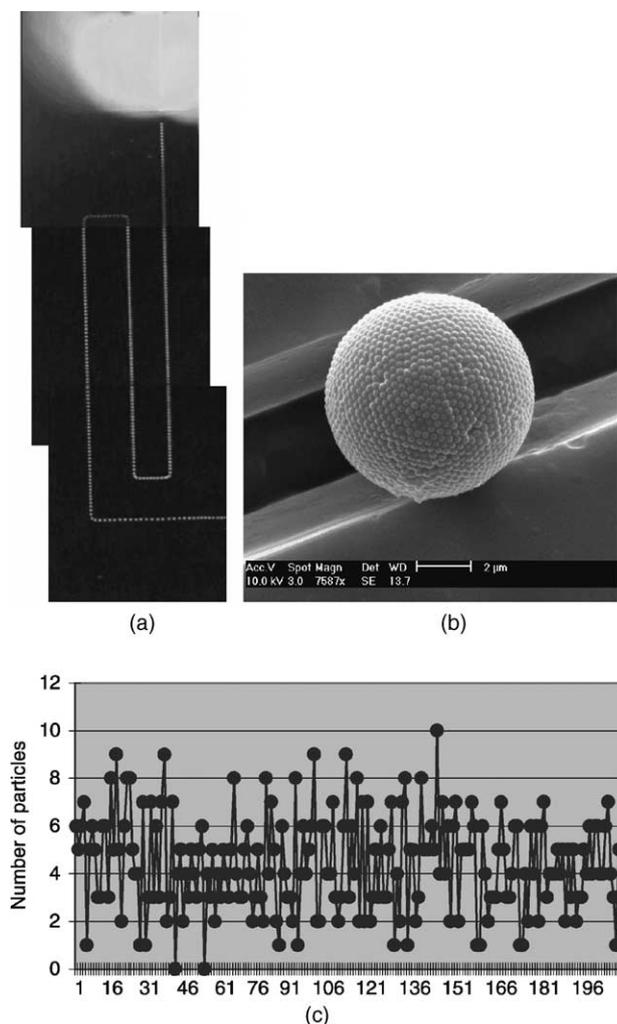


Fig. 4. (a) Optical micrographs of suspension emulsion containing polymer beads with fluorescent dye that were generated at T-type junction and flowing along the channels. (b) Typical scanning electron micrograph of colloidal assemblies that were generated in soft-microfluidic devices. (c) Fluctuation of the number of encapsulated particles in the droplets that were generated consecutively.

laminar flow and the emulsion system without surfactant facilitated water removal from the emulsion droplets to the oil phase. The consolidated particle aggregates were stable against coalescence that would be caused by collision. Optical micrograph in Fig. 4a shows that droplets were generated at T-type junction and flowing along the channel without coalescence, in which 1 μm polymer latex beads with dyes (Fluoresbrite plain YG, Polysciences Inc.) were used for visualization. Their scanning electron micrograph is shown in Fig. 4b.

Particle number density is a very important parameter for developing novel photonic crystals out of our final colloidal aggregates in the future. However, they have statistical variation of the number of particles inside the emulsion droplets [19]. Fig. 4c shows the fluctuation of the average number of particles inside a droplet. For large numbers, the number fluctuation was negligibly small and within a few percent-

ages. For small numbers, however, the number fluctuation of colloidal aggregate became significant and the generated colloidal aggregates were not uniform. The degree of shrinkage of the droplet diameter was dependent on the retention time after the droplet generation, initial droplet diameter, and particle concentration inside a droplet [19].

4. Summary

We have produced uniform spherical colloidal assemblies by removing water from monodisperse suspension emulsions, which were generated by introducing an aqueous particle suspension into a coflowing, surfactant-laden continuous phase using a tapered capillary or soft-microfluidic devices. Our present approach may find uses in photonic crystals, highly reflective paints (or photonic crystals inks), light diffusing materials or, if extended to a smaller scale, in electronic paper [12,20]. For photonic materials, it may be interesting to introduce nanoparticles or reactive sols into the interstices between the latex particles [20].

Acknowledgements

This work has been supported by the BK21 Program, National R&D Project for Nano Science and Technology and Development Project of Next Generation New Technology.

References

- [1] A.D. Dinsmore, J.C. Crocker, A.G. Yodh, *Curr. Opin. Colloid Interface Sci.* 3 (1998) 5.
- [2] O.D. Velev, E.W. Kaler, *Adv. Mater.* 12 (2000) 531.
- [3] E. Snoeks, A. van Blaaderen, T. van Dillen, C.M. van Kata, M.L. Bronersma, A. Polman, *Adv. Mater.* 12 (2000) 1511.
- [4] Y. Lu, Y. Yin, Y. Xia, *Adv. Mater.* 13 (2000) 415.
- [5] P. Jiang, J.F. Bertone, V.K. Colvin, *Science* 291 (2001) 453.
- [6] Z. Zhong, Y. Yin, B. Gates, Y. Xia, *Adv. Mater.* 12 (2000) 206.
- [7] Y. Yin, Y. Lu, Y. Xia, *J. Am. Chem. Soc.* 123 (2001) 771.
- [8] Y. Yin, Y. Xia, *Adv. Mater.* 13 (2001) 267.
- [9] M.S. Fleming, T.K. Mandal, D.R. Walt, *Chem. Mater.* 13 (2001) 2210.
- [10] A.L. Hiddessen, S.D. Rodgers, D.A. Weitz, D.A. Hammer, *Langmuir* 16 (2000) 9744.
- [11] K. Furusawa, O.D. Velev, *Colloids Surf. A* 159 (1999) 359.
- [12] O.D. Velev, A.M. Lenhoff, E.W. Kaler, *Science* 287 (2000) 2240.
- [13] G.-R. Yi, J.H. Moon, S.-M. Yang, *Adv. Mater.* 13 (2001) 1185.
- [14] O.D. Velev, K. Nagayama, *Langmuir* 13 (1997) 1856.
- [15] P.B. Umbanhowar, V. Prasad, D.A. Weitz, *Langmuir* 16 (2000) 347.
- [16] T. Thorsen, R.W. Roberts, F.H. Arnold, S.R. Quake, *Phys. Rev. Lett.* 86 (2001) 4163.
- [17] H. Tamai, A. Fujii, T. Suzawa, *J. Colloid Interface Sci.* 116 (1987) 37.
- [18] G.-R. Yi, V.N. Manoharan, S. Klein, K.R. Brzezinska, D.J. Pine, F.F. Lange, S.-M. Yang, *Adv. Mater.* 14 (2002) 1137.
- [19] G.-R. Yi, T. Thorsen, V.N. Manoharan, M.-J. Hwang, D.J. Pine, S.R. Quake, S.-M. Yang, *Adv. Mater.* 15 (2003), in press.
- [20] F. Iskandar, Mikrajuddin, K. Okuyama, *Nano Lett.* 1 (2001) 231.