

# Fabrication of Colloidal Crystal Beads with Uniform Size by a Drop-Breaking Technique

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In this study, colloidal crystal beads with controllable size, small-size dispersion, and good repeatability were fabricated. These beads have an optical stop-band and can be distinguished by their colors or spectra. Applications in genomics, proteomics, combinatorial chemistry, drug screening, and clinical diagnosis are anticipated.

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Colloidal crystal beads are spherical in shape with a size range of several micrometers and consist of well-ordered monodisperse colloidal nanospheres. Uniform colors can be observed on them by the naked eye when their stop band falls in the visible region. Monodisperse colloidal crystal beads have the potential to serve as materials not only for weak lights but also for high-power lasers. Recently, we noted that the microfluidic technique is a good approach to generating monodisperse emulsions. Based on this technique, a microfluidic drop-breaking method was developed for the fabrication of colloidal crystal beads [1–3], which greatly simplified the fabrication apparatus and improved repeatability. Beads ranging in size from ten micrometers to two millimeters [1] were fabricated to meet different demands.

Figure 1 shows a schematic illustration of the apparatus for generating monodisperse colloidal crystal beads. A small hole was drilled using an excimer pulse laser on the surface of a PTFE pipe, and a fluorinated dispenser needle was inserted into the hole to form a drop-breaking installation. All the junction points were sealed by waterproof glue. Silicone oil KF-96 containing x-22-821 [4] and Span-80 was injected into the PTFE pipe using a syringe pump, and aqueous suspension containing monodisperse silica nanoparticles was driven through the needle by an automation stage whose moving speed was precisely controlled by a computer. The aqueous suspension was cut-off into droplets by the rush of the oil flow at the tip of the needle. The latex drops were collected by a polycarbonate (PC) container rotated slowly to prevent droplets from coalescing during collection. The droplets were heated at 60°C for solvent evaporation. Colloidal crystal beads were obtained overnight and were washed by hexane to remove silicone oil and surfactant.

Bead size and size dispersion are two critical factors affecting the application of the encoded beads in bioassays.

Beads fabricated by this method have good monodispersity. Figure 2 shows an optical image of the beads after solidification. As the beads are highly monodispersed, they can self-assemble to form hexagonal arrays by only putting the beads together [2]. The polydispersities of beads fabri-

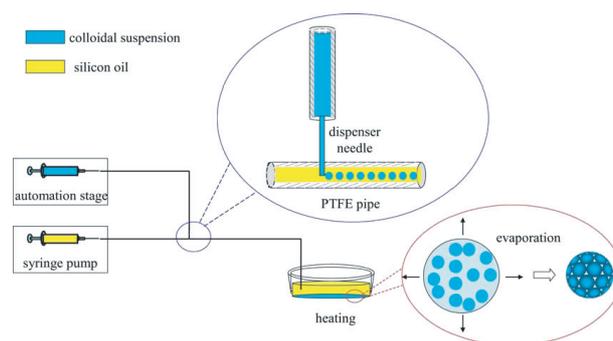


Fig. 1 Schematic representation of apparatus for generating monodisperse colloidal crystal beads.

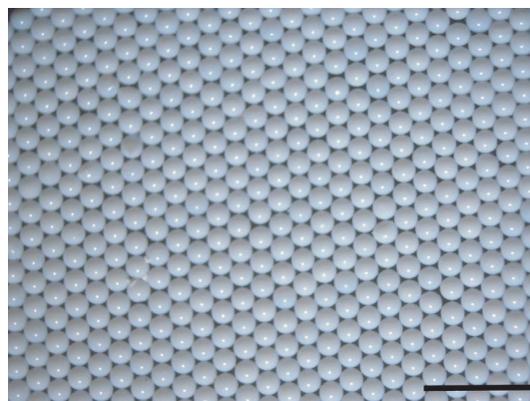


Fig. 2 Picture of uniform colloidal crystal beads derived from drying the suspension droplets. The scale bar is 400 μm long.

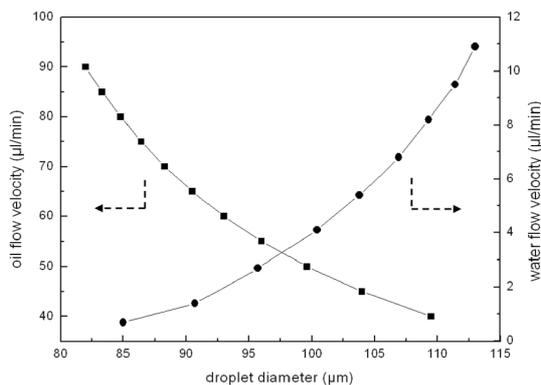


Fig. 3 The relationship between latex droplet size and latex suspension velocity with a constant oil phase flow velocity of 275 μl/min (square-dotted line), and the dependence of latex droplet size on the silicone oil velocity with a constant water phase flow velocity of 3 μl/min (circular-dotted line)

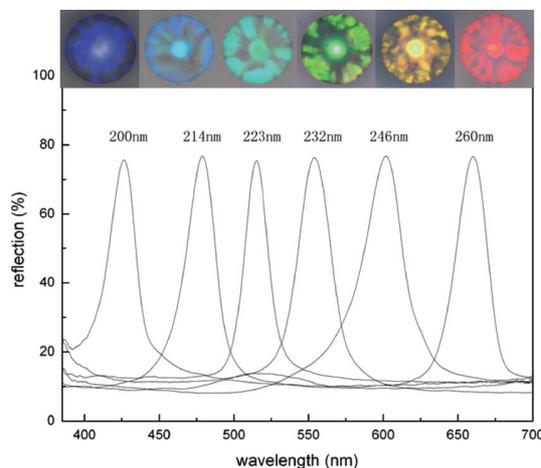


Fig. 4 Reflection spectra and microscopy images of five different colloidal crystal beads in water.

cated by this method were less than 3%. Bead size can be controlled by changing the velocities of the water-phase and oil-phase flows. Figure 3 shows their relationship. From the experimental results, it was clear that both an increase in oil-phase flow velocity and a reduction in the water-phase flow velocity can decrease bead size.

All the beads fabricated under these conditions showed a sharp reflecting peak. Figure 4 shows the reflection spectra of six colloidal crystal beads composed of different-sized silica nanoparticles from 200 nm to 260 nm. In the analyte liquids, beads with reflection peaks in the visible range exhibited brilliant color and can be clearly

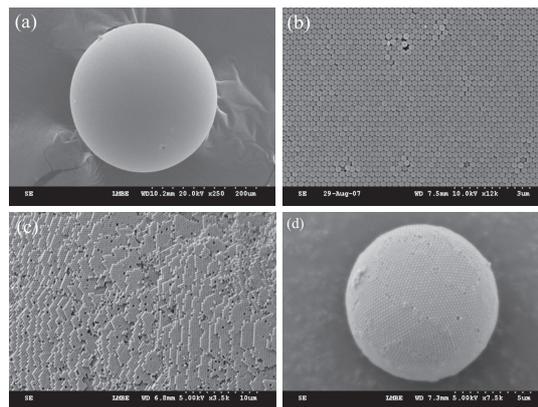


Fig. 5 SEM images of colloidal crystal beads. (a) A low-magnification image of a 200 μm bead. (b) A high-magnification image taken on the surface of the 200 μm bead. (c) An image of a 10 μm bead. (d) The cross section of a bead.

observed by the naked eye. As the colors originate from the ordered periodic structure, they do not suffer from fading, bleaching, quenching, or chemical instability.

The microstructure of a bead with a diameter of 200 μm is shown in Fig. 5 (a). Scanning electron microscopy observation shows the bead has a good spherical shape. Nanoparticles in the beads are hexagonally arranged (Fig. 5 (b)). Such ordering extends from the bead surface to the center, derived from [3] the cross section in Fig. 5 (d). Figure 5 (c) shows the surface microstructure of a bead with a diameter of 10 μm. The distance between the domain boundaries is around three micrometers, while it is over several hundred micrometers in large beads. The decrease in domain size is ascribed to the incurvation of the bead surface. Close-packed cubic (CPC) symmetry was observed in colloidal crystal beads, which is the same structure observed in colloidal crystal films. The formation of CPC symmetry was also supported by the volume change during solvent evaporation.

In conclusion, colloidal crystal beads with diameters ranging from ten micrometers to two millimeters [1] were fabricated by assembling monodisperse colloidal nanoparticles in a water-in-oil system through a drop-breaking method. Applications in metamaterials for high-power lasers are anticipated.

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