MICROFLUIDIC FABRICATION OF COLLOIDAL CRYSTAL FILMS AND SPHERES

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Colloidal crystals, three-dimensional periodic arrays of monodisperse colloidal particles, have attracted considerable attention in the field of materials science and for technological applications because of their novel optical applications as photonic crystals and use as building blocks or templates for fabricating hierarchical structures. Colloidal crystals can be easily prepared by evaporating the solvent from a colloidal suspension placed on a substrate, and hence, in most syntheses, colloidal crystals are formed as a thin film supported by a substrate; this lack of shape variation limits the utility of colloidal crystals in many applications. On the other hand, charged colloids can form crystalline structures with low packing density in a solvent owing to electrostatic repulsion between the colloidal particles. They can freely change shape while preserving their crystalline structure and their morphology can be fixed by polymerizing the gelation reagent added to the colloidal suspension.

In this paper, a method for fabricating self-standing gel films containing highly ordered colloidal crystals and gel spheres containing colloidal crystals is reported. The film-shaped or spherical colloidal crystals are formed using microfluidic techniques and are subsequently immobilized in a hydrogel network by photopolymerization techniques.

An aqueous suspension of monodisperse polystyrene particles (Thermo Fisher Scientific; particle diameter: 198 nm; CV: 5%) or silica particles (Nippon Shokubai Co., Ltd., KE-W20; particle diameter: 210 nm; CV: 7%) was used. The suspension was deionized in vials by using mixed-bed ion-exchange resin (Bio-Rad, AG501-X8) and then mixed with gelation reagents (*N*-methylol-acrylamide (N-MAM) or acrylamide (AAm) as a monomer, *N*,*N*′-methylene-bis-acrylamide (BIS) as a cross-linker, and 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propion amide] (VA) or IRGACURE 2959 as a photoinduced polymerization initiator).

To fabricate a colloidal crystal film with high optical quality, a flat capillary cell was used (Figure 1).[1] The colloidal suspension containing the gelation reagents (particle volume fraction: approximately 10%; N-MAM: 1 M; BIS: 20 mM; VA: 0.5 mM) was forced to flow in the cell (internal dimensions: 0.1 mm thick, 9 mm wide, 50 mm long) by driven with a pressure-regulated air. Above a critical pressure, a momentary strong shear flow was generated, forming

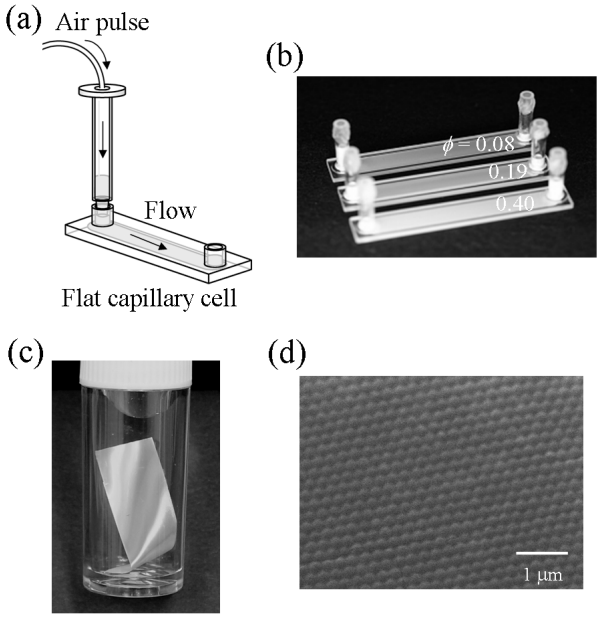

Figure 1 (a) Schematic diagram of the fabrication of a colloidal crystal film. (b) Photograph of flow-aligned colloidal crystal films with different particle concentrations. (c) Photograph of a gel-immobilized colloidal crystal film. (d) SEM image of dried colloidal crystal gel film.

a very uniform and transparent material. Optical characterizations such as ordinary spectroscopy, laser Kossel diffraction, and imaging spectrograph indicate that almost all the capillary space (several square centimeters wide and 0.1 mm thick) was filled with a single-crystal-like domain with a fixed crystallographic orientation determined by the cell geometry. The obtained flow-aligned particle arrays could be immobilized in self-standing gel films by the photopolymerization of the gelation reagents in the suspension.[2] Furthermore, the gel film, which contains water, can be converted into a dry film of densely packed colloidal crystals.[3]

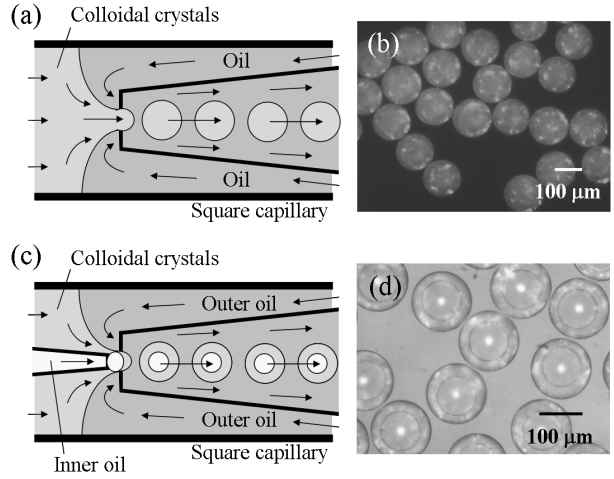

Figure 2 (a) Schematic diagram of the capillary microfluidic device used for generating single emulsions. (b) Optical microscope image of spherical colloidal crystals immobilized in PAAm gels after UV irradiation. (c) Schematic diagram of the capillary microfluidic device for generating double emulsions. (d) Optical microscope image of double emulsions with colloidal crystal shells. The flow rates of the inner oil, middle aqueous, and outer oil phases are 800, 3000, and 10000 μL/h, respectively.

To fabricate microgel spheres containing colloidal crystals, a capillary microfluidic device was used (Figure 2).[4] The colloidal suspension containing the gelation reagents was pumped from one end of the outer capillary while silicone oil with a surfactant (Dow Corning 749) was pumped from the opposite end into the orifice of the inner tapered collection tube. The oil phase hydrodynamically focuses the colloidal suspension, which breaks up at the orifice of the collection tube to form monodisperse droplets containing colloidal crystals. By properly adjusting the flow rates, monodisperse droplets could be formed. After UV irradiation, the colloidal crystals in the droplets could be immobilized in the gel spheres preserving the crystalline structure of the colloids.

Furthermore, by injecting another oil from a capillary added to the device, droplets with colloidal crystal shells could be formed (Figures 2(c) and (d)).[5] After UV irradiation, the colloidal crystal shells could be immobilized in the gel network, preserving their crystalline structure. If stimuli-sensitive gels are used for immobilizing the colloidal crystals, the color effect or wavelength of light that is observed because of Bragg diffraction can be altered by external stimuli. Therefore, these materials are potentially useful as labels and sensors for monitoring chemical reactions or environmental changes through observations of the Bragg diffraction color or wavelength.

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