Fabrication of Tunable Spherical Colloidal Crystals Immobilized in Soft Hydrogels

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Spherical colloidal crystals are three-dimensional periodic arrays of monodisperse colloidal particles with a spherical geometry.\textsuperscript{[1]} The spatial periodicity of the refractive index of the colloidal crystalline arrays results in a photonic band gap effect, and hence, they act as photonic crystals in the optical regime.\textsuperscript{[2]} In contrast with conventional film-type colloidal crystals where the crystals are aligned by the film, the photonic band gap of spherical colloidal crystals is independent of the rotation under illumination of the surface at a fixed incident angle of the light.\textsuperscript{[3]} Therefore, spherical colloidal crystals are potentially useful not only for conventional photonic crystal applications, but also as a new type of spectrum-encoding carrier for biomolecular screening,\textsuperscript{[4]} non-bleachable color pigments,\textsuperscript{[5]} and refractive color displays\textsuperscript{[6]}. Spherical colloidal crystals can be fabricated using droplets as templates; droplets of aqueous colloidal suspension are dispensed on a hydrophobic surface or in oil and then dried. The evaporation of the liquid medium leads to the assembly of particles into close-packed structures with a spherical geometry. Since upon drying the particles touch one another, the crystal lattice constant is uniquely determined by the diameter of the particles. Therefore, fabrication of colloidal crystals with different wavelengths for their photonic band gap requires colloidal particles with different size or refractive index. It is difficult to tune the diffraction wavelength after the colloidal crystal spheres are formed; this lack of tunability limits the utility of these structures for many practical applications.

An alternate route to the formation of spherical colloidal crystals that may overcome the limitations in tunability is through the use of charged colloids. They can form crystalline structures but with a lower packing density in a liquid medium due to their repulsive electrostatic interaction between the particles.\textsuperscript{[7]} Since the charged colloidal particles do not touch, the lattice constant can readily be tuned by changing the particle volume fraction. The wavelength of the photonic band gap can also be manipulated by immobilizing these crystals in a soft hydrogel;\textsuperscript{[8]} then the wavelength of the photonic band gap can be altered on-demand if a stimuli-sensitive hydrogel is used. By adjusting the volume of the hydrogel through an
external stimulus, the lattice constant of the crystals can be tuned accordingly; this is useful for applications such as tunable photonic crystals,[9] tunable lasers,[10] and biological and chemical sensors.[11] Despite such attractive features, few studies on spherical colloidal crystals with low packing density have been reported,[12] and fabrication of spherical colloidal crystals with a tunable band-gap wavelength has not been developed.

In this communication, we demonstrate that gel-immobilized colloidal crystal spheres can be fabricated through the combination of microfluidics[13] and photo-polymerization. These colloidal crystal spheres differ from conventional ones in two aspects: First, the wavelength of their photonic band activity is not uniquely determined by the size of the colloidal particles; instead, it can be adjusted by simply varying the particle concentration before polymerization. Second, the wavelength of the photonic band activity is also controlled by external stimuli, such as temperature. Thus the wavelength can be tuned even after the colloidal crystal spheres are formed. These features have great practical advantages.

The process for fabricating the gel-immobilized colloidal crystal spheres is illustrated schematically in Scheme 1. Our microfluidic device has a flow-focusing geometry to generate monodisperse water-in-oil (W/O) emulsions. The water phase is pumped from one end of the outer square capillary while the oil phase flows from the opposite end into the orifice of the inner tapered collection tube. The oil phase hydrodynamically focuses the aqueous phase, which breaks up at the orifice of the collection tube to form monodisperse W/O droplets. The aqueous phase consists of charged polystyrene particles with a diameter of 198 nm, as well as a monomer, a cross-linker, and a polymerization initiator for photo-polymerization. The quiescent particles are in a crystalline state and retain their crystalline state upon formation of the emulsion drops. The oil phase is a poly(dimethylsiloxane) oil (PDMS) with a surfactant (Dow Corning 749) to stabilize the oil-water interfaces without destroying the crystalline state of the charged colloids. The solutions were filtered and then infused into the microfluidic device. After formation, the emulsion droplets were irradiated with UV light to photo-
polymerize the aqueous droplets, thereby immobilizing the colloidal crystals in the polyacrylamide (PAAm) hydrogel.

**Scheme 1.** Schematic of the procedures used for fabrication of gel-immobilized colloidal crystal spheres using capillary microfluidics and photo-polymerization. The water phase is an aqueous suspension of charged polystyrene particles containing gelation reagents. The oil phase is a PDMS oil with a surfactant. The device is irradiated with UV light to polymerize the hydrogel and immobilize the loosely-packed colloidal crystals in the network, forming the colloidal crystal spheres.

By properly adjusting the conditions for fabrication, including the surfactant concentration, the gel-reagent concentration, the particle concentration and the time of UV irradiation, stable monodisperse emulsions can be formed (**Figure 1(a)**). The colloidal crystals in the water droplets can be immobilized in PAAm hydrogel spheres after UV irradiation, preserving the crystalline structure; this is evident from the diffraction colors shown in **Figure 1(b)**. The size of the gel spheres is determined by that of the pre-gel droplets, which can be controlled by adjusting the relative flow rates of the fluids or the size of the capillary orifice.[13] Since the
gel-immobilized colloidal crystal spheres are soft, they are deformable under compression between glass slides, as shown in Figure 1(c).

**Figure 1.** (a) Formation of water droplets with colloidal crystals in the microfluidic device. The flow rates of the inner aqueous and outer oil phases are 2000 and 1000 µL h⁻¹, respectively. (b) Optical microscope image of the spherical colloidal crystals immobilized in PAAm hydrogels after UV light irradiation. (c) Optical microscope image of PAAm-immobilized colloidal crystal spheres deformed under compression.

Upon illumination by visible light, the gel-immobilized colloidal crystal spheres show the characteristic colors of diffraction patterns;[3, 14] a bright spot can be seen at the center of the sphere while many spots or lines on series of concentric rings can also be observed (Figure 2(a)-(c)). Since the packing density of charge-stabilized colloidal crystals is adjustable, the diffraction colors or photonic crystal wavelengths can be tuned by varying the concentration of particles in the droplets before gelation (Figure 2(a)-(d)). The peak in the reflection spectrum at normal incidence corresponds to the bright dot at the center, and is due to Bragg
diffraction from the (111) lattice planes of a face-centered-cubic (FCC) structure aligned parallel to the spherical surface. The Bragg condition for normal incidence is

$$\lambda = 2n_c d_{111}, \quad (1)$$

where $\lambda$ is the Bragg wavelength, $n_c$ is the refractive index of the colloidal crystals, and $d_{111}$ is the interplanar spacing of FCC (111) lattice planes. The value of $d_{111}$ for the FCC structure can be estimated from geometrical considerations using the particle volume fraction, $\phi_p$ and the particle diameter, $d$, and is given by

$$d_{111} = \left( \frac{2 \pi}{9 \sqrt{3} \phi_p} \right)^{1/3} d \quad (2).$$

The volume-weighted average of the refractive indices of the components provides a good approximation of $n_c$,[15]

$$n_c = n_p \phi_p + n_{gel} \phi_{gel}, \quad (3)$$

where $n_p$ and $n_{gel}$ are the refractive indices of the polystyrene particles ($n_p = 1.59$) and hydrogel, respectively, and $\phi_{gel}$ is the gel volume fraction. Since the hydrogel is composed of polymer and water, the refractive index of the gel can be approximated as $n_{gel} = n_{pol} \phi_{pol} / \phi_{gel} + n_w \phi_w / \phi_{gel}$, where $n_{pol}$ and $n_w$ are the refractive indices of the polymer ($n_{pol} = 1.45$)[16] and water ($n_w = 1.33$), respectively, and $\phi_{pol}$ and $\phi_w$ are the volume fraction of the polymer and water.

Using the observed peak wavelength in Fig. 2(d), the polymer concentration ($\phi_{pol} = 0.26 \phi_p$) and the assumed refractive index of the gel, the particle volume concentration of the colloidal crystals in Fig. 2(a)-(c) is calculated to be 31%, 46%, and 59%, respectively.
Figure 2. Photograph of the PAAm-immobilized colloidal crystal spheres with different particle concentrations under light at normal incidence. (a) $\phi_p = 0.31$, (b) $\phi_p = 0.46$, (c) $\phi_p = 0.59$. (d) Normal reflection spectra of the PAAm-immobilized colloidal crystal spheres. The scale bars in (a-c) are 50 $\mu$m.

This technique for fabricating gel-immobilized colloidal crystal spheres is applicable to various stimuli-sensitive hydrogels that swell or shrink in response to the external stimuli. For example, a colloidal crystal sphere immobilized in a poly(N-isopropylacrylamide) (PNIPAm) gel is shown in Figure 3. The PNIPAm gel is a thermosensitive polymer that undergoes a volume transition at a lower critical solution temperature of 32 °C.\textsuperscript{[17]} Upon heating from 22 to 40 °C, the PNIPAm-immobilized colloidal crystal sphere begins to shrink rapidly at around 32 °C, resulting in a change in the diffraction color and Bragg diffraction wavelength. By contrast, PAAm-immobilized colloidal crystal spheres do not exhibit such thermosensitivity. The particle volume fraction of the PNIPAm-immobilized colloidal crystal sphere at each
temperature can be estimated from the particle volume in the sphere (8.9×10^{-13} \text{ m}^3) and the sphere diameter (Figure 3(c)). By substituting the calculated particle volume fraction, the PNIPAm gel volume fraction ($\phi_{\text{pol}} = 0.16\phi_0$), and the assumed refractive index of PNIPAm ($n_{\text{pol}} = 1.50$) into equations (1), (2), and (3), the Bragg diffraction wavelengths are estimated and shown as filled triangles, ▲, in Figure 3(d). The estimated values are in excellent agreement with the observed Bragg diffraction wavelengths.

Figure 3. (a) Microscope images of the reflection at normal incidence of a thermosensitive PNIPAm-immobilized colloidal crystal sphere at various temperatures. (b) Reflection spectrum at normal incidence of the PNIPAm-immobilized colloidal crystal sphere at various temperatures. (c) A plot of the diameter of the gel-immobilized colloidal crystal spheres as a function of temperature. (●: PNIPAm-immobilized colloidal crystal sphere, ○: PAAm-
immobilized colloidal crystal sphere) (d) A plot of the wavelength of Bragg reflection for the gel-immobilized colloidal crystal spheres as a function of temperature. (●: experimentally measured Bragg wavelength of PNIPAm-immobilized colloidal crystal sphere, ▲: calculated Bragg wavelength of PNIPAm-immobilized colloidal crystal sphere, ○: experimentally measured Bragg wavelength of PAAm-immobilized colloidal crystal sphere, Δ: calculated Bragg wavelength of PAAm-immobilized colloidal crystal sphere) The curves in (c) and (d) are guides to the eye.

In summary, we have fabricated colloidal crystal spheres with tunable photonic wavelengths at low packing density by immobilizing colloidal crystals in soft hydrogels. This new material has great potentials for optical applications. In particular, since colloidal crystals are non-toxic and not susceptible to photo-bleaching, our colloidal crystal spheres are potentially useful as labels for biomolecular screening\textsuperscript{[4]} and as biological and chemical sensors for monitoring chemical reactions or the changes in the environments through the Bragg diffraction wavelength or diffraction color\textsuperscript{[11]}.

**Experimental Microfluidics:** A detail description of the fabrication techniques of glass microcapillary devices has been described in ref. 13. Round glass capillary tubes (World Precision Instruments) with outer and inner diameters of 1.0 mm and 580 μm respectively were tapered to the desired diameter using a capillary puller (Sutter Instrument, P-97) and a microforge (Narishige, MF-830). The orifice sizes affect the dimensions of the emulsions formed. The inside of the round tapered capillaries was coated with a hydrophobic reagent (GELEST. Inc., Tridecafluoro-1,1,2,2-tetrahydroctyl-triethoxy silane). The round capillary was then fitted into
the square capillary (Atlantic International Technology), which had an inner dimension of 1.0 mm. A transparent epoxy resin was used to seal the tubes where required.

To generate the W/O emulsions to form the microgel spheres containing the colloidal crystals, we used an aqueous suspension of charged polystyrene particles; the quiescent particles form a crystalline state. We added gelation reagents including a monomer, a cross-linker, and a polymerization initiator to the aqueous phase. Polystyrene latex (Duke Scientific Corp., particle diameter 198 nm; standard deviation 3 %) was deionized using a mixed-bed ion-exchange resin (Bio-Rad, AG501-X8) in vials until the suspension showed iridescence indicative of a colloidal crystal phase. To immobilize the particle arrays in hydrogel spheres, the suspension was mixed with aqueous solutions of acrylamide (1 M, Sigma-Aldrich) as a monomer, \( N,N' \)-methylene-bis-acrylamide (20 mM, Fluka) as a cross-linker, and a photoinitiator (0.2 wt%, Ciba, IRGACURE 2959). For fabrication of thermosensitive hydrogel spheres, \( N \)-isopropylacrylamide (0.5 M, Sigma-Aldrich), \( N,N' \)-methylene-bis-acrylamide (10 mM), and a photoinitiator (0.2 wt%, Ciba, IRGACURE 2959) were dissolved in the suspension. The oil phase was a poly(dimethylsiloxane) fluid (50 cSt, Sigma-Aldrich) containing a surfactant (2 wt%, Dow Corning 749) to stabilize the interface between the water and oil phases without destroying the crystalline state of the colloids. These solutions were filtered with 5-micron filters to remove particulate impurities and then infused into the microfluidic device through polyethylene tubing (Scientific Commodities) attached to syringes (SGE) that were driven by positive displacement syringe pumps (Harvard Apparatus, PHD 2000 series). The formation of droplets was monitored with a high-speed camera (Vision Research) attached to an inverted optical microscope (Leica, DMIRB). The droplets formed in the capillary device were irradiated by a UV lamp (UVP, UVG-54) to polymerize the gelation reagents dissolved in the suspension. The polymerized microgel spheres filled with colloidal crystals were removed from the PDMS oil and washed with isopropanol to remove any adsorbed oil. The microgel spheres were then washed and stored in water.
Characterization: The normal reflection spectra of the microgel spheres with colloidal crystals were measured using a fiber optic spectrometer (Ocean Optics Inc., HR2000+) attached to an optical microscope (Nikon, ECLIPSE TE2000-E). The temperature of the sample was controlled using a temperature controller (Physitemp, TS-4 ER).

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Keywords (Colloids, Photonic Crystals, Hydrogels, Microfluidics, Stimuli-Responsive Materials)

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Title (Fabrication of Tunable Spherical Colloidal Crystals Immobilized in Soft Hydrogels)

We report a method for fabricating gel-immobilized colloidal crystal spheres using microfluidics. The diffraction color or photonic wavelength of the gel-immobilized colloidal crystal spheres can be adjusted by varying the particle concentration before gelation and tuned by external stimuli after preparation.