Liquid Crystals Hot Paper

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Reconfigurable Photonic Capsules Containing Cholesteric Liquid Crystals with Planar Alignment

*Sang Seok Lee, Su Kyung Kim, Jong Chan Won, Yun Ho Kim, and Shin-Hyun Kim**

Abstract: *Cholesteric liquid crystals (CLCs) reflect selected wavelengths of light owing to their periodic helical structures. The encapsulation of CLCs leads to photonic devices that can be easily processed and might be used as stand-alone microsensors. However, when CLCs are enclosed by polymeric membranes, they usually lose their planar alignment, leading to a deterioration of the optical performance. A microfluidics approach was employed to integrate an ultrathin alignment layer into microcapsules to separate the CLC core and the elastomeric solid membrane using triple-emulsion drops as the templates. The thinness of the alignment layer provides high lubrication resistance, preserving the layer integrity during elastic deformation of the membrane. The CLCs in the microcapsules can thus maintain their planar alignment, rendering the shape and optical properties highly reconfigurable.*

The helical structure of cholesteric liquid crystals (CLCs) leads to the periodic modulation of the refractive index along the helical axis, which yields a photonic stop band.[1] In particular, when the product of the chiral pitch and the refractive index is comparable to the wavelength of visible light, CLCs exhibit structural colors through the selective reflection of circularly polarized light at the stop band. Moreover, the bandgap can be dynamically modulated with external stimuli.[2,3] Such inimitable optical properties make CLCs appealing for reflection-mode displays,[4,5] laser resonators,[6] and thermometers.[7,8] To facilitate their processing and reconfigurability for various applications or to create stand-alone microsensors, CLCs have been encapsulated within polymeric membranes. Typically, oil droplets of the liquid crystals (LCs) in water are enclosed by polyurea or gelatin through emulsification polymerization.[9,10] However, such approaches only achieve limited control over the capsule size and membrane properties. Although microcapsules prepared by layer-by-layer deposition on colloidal templates have served as uniform LC containers,[11] the low efficiency of encapsulation restricts their applications. More importantly, both approaches provide thin and fragile polymeric membranes that are susceptible to rupture under mechanical stress. Microfluidic technologies have enabled the controlled formation of double-emulsion drops, which have recently been used as templates for creating uniform and robust CLC capsules with high encapsulation efficiency;[12] double-emulsion drops have also been used to make liquid or solid shells of liquid crystals to be used in omnidirectional lasers or micropumps.[13,14] Nevertheless, the molecular orientation on the surface of the polymeric membrane is uncontrolled. This leads to a deterioration of the optical performance and frequently causes problems preventing their use in photonic applications, including omnidirectional lasing. Furthermore, the membrane is mechanically stable, but inflexible, rendering the capsule shape poorly reconfigurable. Therefore, CLC encapsulation methods that simultaneously achieve controlled molecular orientation and membrane elasticity remain to be in great demand.

Herein, we report a microfluidics-based approach for the controlled formation of photonic microcapsules that contain CLCs with planar alignment and can be dynamically reconfigured. With a glass-capillary microfluidic device with precisely controllable wettability, we prepared oil-in-water-in-oil-in-water (O/W/O/W) triple-emulsion drops with an ultrathin inner water shell through single-step emulsification. The triple emulsion consists of an innermost CLC core, a water alignment shell, a photocurable oil shell, and a continuous water phase. The liquid-crystal molecules in the core display planar alignment along the interface with the inner water shell supported by the ultrathin water shell, which was further encapsulated by an elastic polymer membrane through photopolymerization of the outer shell. Owing to the radial orientation of the helical axes, the resultant microcapsules exhibit omnidirectional structural colors that are much more pronounced than in CLC capsules formed from O/O/W double-emulsion drops without the alignment shell. Furthermore, when such microcapsules are used in array, strong photonic cross-communication is observed.[15] Moreover, the photonic microcapsules can be elastically deformed while the planar alignment is maintained, rendering both the optical properties and the capsule shape highly reconfigurable.

The liquid-crystal molecules prefer to align parallel to the interface with water.[16] When poly(vinyl alcohol) (PVA) is included in the water phase, it is located at the interface and promotes the planar alignment.[17,18] This boundary effect of the planar alignment promotes the arrangement of the CLCs with a helical axis perpendicular to the interface, which leads to striking reflection colors. For the CLC molecules to adopt a planar alignment within the microcapsules, double-shell

[*] S. S. Lee, Prof. S.-H. Kim
Department of Chemical and Biomolecular Engineering
Korea Advanced Institute of Science and Technology
Daejeon, 305-701 (Korea)
E-mail: kim.sh@kaist.ac.kr
S. K. Kim, Dr. J. C. Won, Dr. Y. H. Kim
Center for Advanced Functional Polymers
Korea Research Institute of Chemical Technology
Daejeon, 305-600 (Korea)

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structures are required; the inner shell is an aqueous PVA solution that induces the planar alignment, and the outer, solid shell stabilizes the inner alignment layer. To accomplish this, we used triple-emulsion drops with intrinsic core–shell–shell geometry that serve as perfect templates for creating CLC capsules with controlled molecular alignment. The thickness of the inner shell insignificantly influences the molecular alignment, and therefore, a thinner shell is preferred as a photonic CLC with a larger volume can thus be used. Although distinct microfluidic approaches for the synthesis of triple-emulsion drops have been reported,[19–21] none of them are adequate for this purpose. We thus designed a new capillary microfluidic device that combines two distinct double-emulsion makers (Figure 1a), which are based on concurrent core–sheath flow[22] and countercurrent flow, respectively.[23]

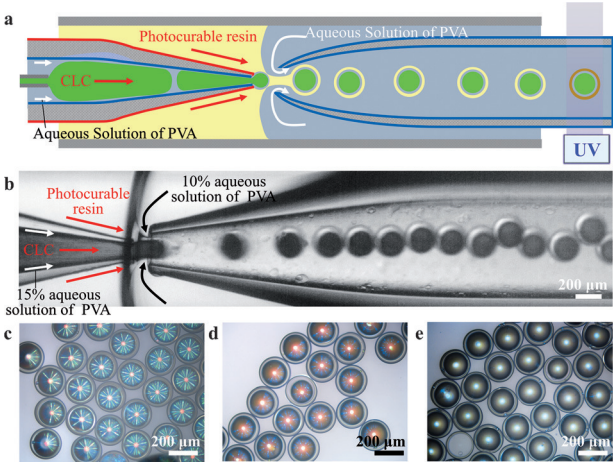

Figure 1. a,b) Schematic representation and optical microscope (OM) image of the capillary microfluidic device used for the production of the O/W/O/W triple-emulsion droplets consisting of a CLC innermost core, an aqueous middle shell with 15 wt% PVA, an outermost oil shell of photocurable resin, and a continuous aqueous phase with 10 wt% PVA. The inner wall of the injection capillary is hydrophilic (blue), and the outer wall is hydrophobic (red), whereas all surfaces of the collection capillary were treated to be hydrophilic. c–e) OM images of microcapsules taken in the reflection mode without polarizers. Their CLC cores have three different chiral-dopant concentrations, which leads to different bandgap positions.

The device consists of two tapered cylindrical capillaries nested in a square capillary. One cylindrical capillary with an orifice diameter of 160 μm was carefully treated to have a hydrophilic inner wall and a hydrophobic outer wall, whereas the other capillary, with an orifice diameter of 240 μm, only features hydrophilic surfaces. An additional small capillary is inserted through the untapered opening of the capillary with the smaller orifice. A CLC solution of the host LC (BHR-59001) containing a chiral dopant is injected through the additional small capillary, and a 15 wt% aqueous solution of PVA is injected through the untapered opening of the capillary with the smaller orifice; this PVA concentration was chosen as it leads to a small viscosity mismatch with the CLC core and minimizes fluctuations in the flow rate during device operation. Therefore, these two immiscible fluids simultaneously flow through the capillary. Owing to the hydrophilic nature of the inner wall, the aqueous PVA solution flows along the wall while the CLC solution forms a train of long emulsion drops that flow through the center of the channel without touching the wall. This leads to the formation of a discontinuous core–sheath flow in the capillary. A photocurable precursor for silicone rubber is injected through the interstice between the cylindrical capillary and the square capillary, which wets the hydrophobic outer wall of the cylindrical capillary. At the same time, a 10% (w/w) aqueous PVA solution is injected through the interstices between the cylindrical capillary with the larger orifice and the square capillary as a countercurrent flow. The continuous phase is coaxially focused into the orifice of the cylindrical capillary, which leads to the breakup of all fluids into triple-emulsion drops (Figure 1b; see also the Supporting Information, Movie S1); the ultrathin inner shell is not discernable in the optical microscopy images. The triple-emulsion drops are continuously irradiated with ultraviolet (UV) light during collection in a glass vial containing 5.5 wt% aqueous solution of PVA, resulting in polymerization of the outer photocurable resin shell to form an elastic solid shell (Figure 1c–e); direct UV irradiation in the device can cause clogging of the channel. Although triple-emulsion drops and double-emulsion drops without a CLC core are repeatedly produced, the CLC capsules with an average density of 1.050 sediment in the 5.5% PVA solution with a density of 1.009, while the double-emulsion drops with an average density of 1.002 remain suspended in the same solution. Therefore, the CLC microcapsules are spontaneously separated from the mixture without any post-processing (see Figures S1 and S2).

The resultant microcapsules are composed of a CLC core, an inner alignment shell, and an outer silicone membrane (Figure 2a). The alignment shell was designed to be ultrathin, and its thickness was indirectly measured by scanning electron microscopy (SEM). For this, the water was fully evaporated from the microcapsules to consolidate the PVA in the shell; the silicone membrane is water-permeable. The silicone membrane was then cleaved with a razor blade, and the CLC core was removed by washing with isopropyl alcohol several times; the consolidated PVA is not dissolvable in isopropyl alcohol. The cleaved membrane with an average thickness of 17.7 μm has a 298 nm thick PVA film on the inner surface (Figure 2b). From the thickness of the dried PVA layer, the thickness of the alignment shell before water evaporation could be estimated to be 1.99 μm assuming volume conservation; the PVA volume fraction in the 15 wt% PVA solution was estimated to be 15% (v/v), and the water shell is therefore 6.67 times thicker than the dried PVA layer.

The CLC cores enclosed by aqueous shells exhibited striking reflection colors owing to the radial orientation of the helical axes caused by planar alignment at the interface (Figure 2c–e). The optical performance does not deteriorate when the CLCs are encapsulated with a double shell in comparison with CLC drops directly dispersed in aqueous PVA solution (Figure S3). Each microcapsule features a bright central spot that is due to normal reflection at the stop band wavelength; the wavelength λ is given by the

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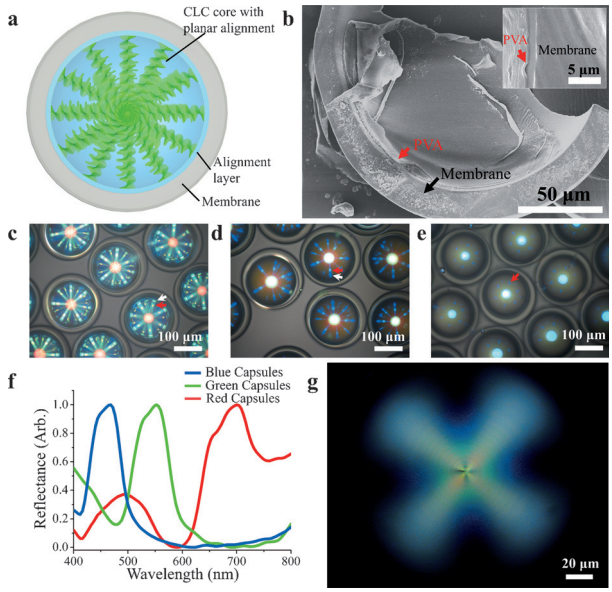

Figure 2. a) Schematic representation of a double-shell microcapsule with a CLC core with radially aligned helices. b) Scanning electron microscopy (SEM) image of a blade-cut microcapsule where the CLC core was removed prior to drying. The inset shows the thicknesses of the elastic membrane and the dried PVA film. c–e) OM images of CLC microcapsules with three different bandgap positions taken in the reflection mode without polarizers. Photonic cross-communication with their neighbors leads to the color patterns indicated by the white and red arrows. f) Normalized reflectance spectra of the CLC microcapsules in (c–e). g) Cross-polarized OM image of a CLC microcapsule taken in transmission mode showing a cross pattern and a series of concentric rings. All microscope images were taken in reflection mode.

product of the chiral pitch p and the effective refractive index n_{eff}. When the microcapsules were used in array, additional color patterns around the central spot were observed that are due to photonic cross-communication with their neighbors.[15] Incident light that impinges with an angle of 45° is reflected to be parallel to the substrate, and then reflected again by the neighboring microcapsules with an angle of 45° to be perpendicular to the substrate (Figure S4 a).[15,24] Although the microcapsules have polymer membranes with a refractive index of 1.419, which is different from that of water, dual refraction at the outer and inner interfaces has no net influence on the reflection angle. This reflection at an angle of 45° results in green and blue patterns for red and green microcapsules, respectively, as indicated by the white arrows in Figure 2 c, d; this finding is consistent with the reflection wavelength at an angle of 45°, $\lambda \cos 45°$; no patterns are observed for the blue microcapsules in Figure 2 e as the wavelength for the 45° reflection is in the UV range. The pattern has as many lines as the microcapsules have neighboring microcapsules; the lines are observed instead of spots upon defocusing (Figure S5). Furthermore, the microcapsules exhibit spots with different colors, as indicated by the red arrows. They originate from a triple-reflection process: A beam reflected at the surface of the CLC core is reflected again at the free interface between water and air, and then reflected at the surface of the CLC core in a neighboring microcapsule to be perpendicular to the free interface (Figure S4 a).[15] For two microcapsules in contact immediately below the air–water interface, the reflection angle becomes 31.1°, which is consistent with the distance between the spot and the center of the CLC core; the distance relative to the core radius (43.9 μm/85 μm) is coincident with $\sin 31.1°$, confirming that the spots are caused by triple reflection. The reflection angle and the distance between spot and center depend on the water level and the separation between the microcapsules (Figure S4 b, c). The colors of the spots for red, green, and blue microcapsules are orange, sky blue, and blue, respectively, which is also consistent with $\lambda \cos 31.1°$.

Reflectance spectra of the microcapsules are shown in Figure 2 f. The main peaks are located at wavelengths of 700, 552m, and 468 nm for the red, green, and blue microcapsules respectively, and are due to normal reflection at the stop band with $\lambda = p\, n_{\text{eff}}$. A second peak is only observed for the red microcapsules and appears at a wavelength of 495 nm, which is coincident with $\lambda \cos 45° = 495$ nm. The second peaks from the 45° reflection for the green and blue microcapsules are expected at wavelengths of 390 nm and 330 nm, respectively, which are out of the measurement range. There are no discernable peaks corresponding to the 31.1° reflection for all microcapsules owing to their low intensity. These reflectance spectra and the photonic cross-communication indirectly imply that the helical axes of the CLCs in the core are radially oriented. We further confirmed the radial orientation using an optical microscope equipped with crossed polarizers. The image thus obtained shows a cross pattern and a series of concentric rings around a small cross pattern at the center (Figure 2 g). These cross patterns and concentric rings are typical evidence of radially oriented helical axes.[25,26]

To compare the optical performance of CLCs with planar alignment with unaligned ones, we prepared microcapsules without the aqueous alignment shell from O/O/W double-emulsion drops; the direct contact between the CLC core and the silicone membrane yields helical axes with random orientation. The two microcapsules look substantially different when studied with an optical microscope in reflection mode (Figure 3 a, inset). The isolated microcapsule with the alignment layer shows a bright central spot of green color and negligible reflection from the side. In contrast, the microcapsule containing the same CLC but no alignment layer shows a weak and inhomogeneous green color across the whole CLC core. Reflectance spectra obtained from the central parts of both microcapsules placed in the field stop of the optical microscope further clarify the difference. The CLC microcapsule with the alignment layer shows 30.3 % reflectivity, even though the reflection occurs only from 66.7 % of the field stop area (Figure 3 a); the reflectivity was determined from the peak height. This result implies that the reflectivity is as high as 45.5 % when only the central spot area is included in the measurement; the maximum reflectivity achievable with CLCs is 50 % because only circularly polarized light with the same handedness is reflected by the helical photonic structure. In contrast, the CLC microcapsule without the alignment layer shows a reflectivity of only 13.7 % even though reflection occurs over the whole area of the field stop.

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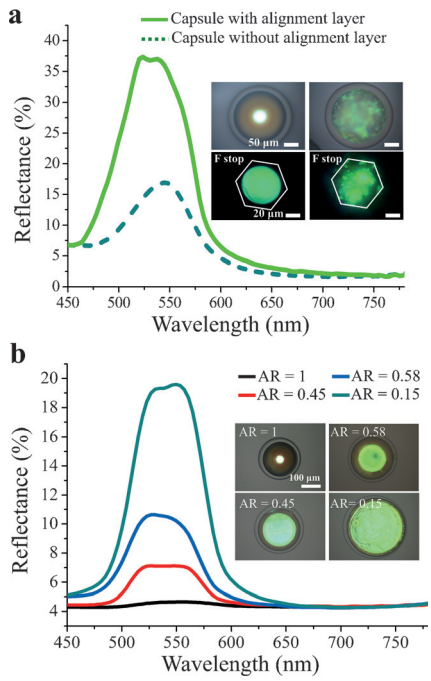

Figure 3. a) Reflectance spectra of the microcapsules with (——) and without (-----) the alignment layer. Insets: Corresponding OM images where the field stops are indicated by white hexagons. b) Reflectance spectra of single microcapsules deformed to four different aspect ratios (the height relative to the diameter of the deformed microcapsule). Insets: Corresponding OM images for each AR value. All OM images were taken in reflection mode without polarizers.

The outer shell of the microcapsules is made of flexible silicone rubber, enabling the elastic deformation of the microcapsules under mechanical stress. For example, green microcapsules were deformed into circular discs when squeezed with a pair of glass slides (Figure 3b, inset; for a series of optical microscopy images showing similar compression experiments with green, red, and blue microcapsules, see Figure S6). During the deformation process, the ultrathin alignment layer spreads over the inner surface of the silicone shell while enclosing the CLC core, thereby maintaining the planar alignment of the molecules. The thinness of the alignment layer provides strong lubrication resistance, preventing direct contact between the CLC and the silicone wall during the deformation.[27,28] Moreover, the thin shell ensures that the CLC cores become instantaneously deformed. The compression leads to an increase in the flattened area at which the helical axis is vertically oriented, resulting in an increase in reflectivity (Figure 3b). The reflectivity is increased by a factor of 8.8 when the microcapsules are deformed to have an aspect ratio (AR) of 0.58. On further deformation to ARs of 0.45 and 0.15, the reflectivity increased by factors of 18.7 and 47.6, respectively; these factors are roughly in line with the ratio of the flattened area to the bright central area of the spherical microcapsule. The CLCs in the microcapsules maintain their planar alignment during the deformation and recover their original radial configuration as soon as they are relaxed from the compression (Movie S2). Although the time scale of the recovery process is difficult to estimate, we expect from the movie that recovery occurs within less than 100 ms. This is impossible to achieve with single CLC drops stabilized with PVA in water, which coalesce under the same compression (Figure S7). At a higher deformation with AR = 0.13, the alignment shell is not able to separate the CLC core from the silicone membrane, resulting in inhomogeneous textures in the deformed and recovered microcapsules (Figure S8a, b).

The reconfigurability of the microcapsules can be maintained even in air when their alignment layer is composed of a mixture of water and glycerol (92:8, v/v) containing 12.5 wt% PVA. Although water slowly evaporates from the layer, glycerol is nonvolatile and remains in the layer, thereby supporting the stable planar alignment of the CLC core[29] in air (Figure 4a–c); the dried microcapsules maintain the planar alignment during elastic deformation (Figure S9).

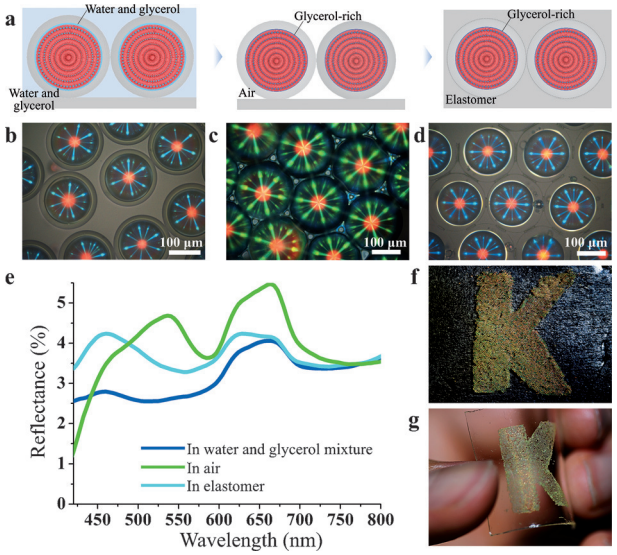

Figure 4. a) Schematic representation showing the removal of the continuous phase and the formation of a photonic film with an embedded CLC drop. b–d) OM images of CLC microcapsules with an alignment layer consisting of a water/glycerol mixture that were dispersed in this mixture (b), air (c), or in an elastomer (d). All images were taken in reflection mode without polarizers. e) Reflectance spectra of the CLC microcapsules in (b–d). f, g) Photographs of the flexible photonic film.

The air environment leads to a color change of the photonic cross-communication with double reflection, while no color change was observed for the normal reflection at the center of the microcapsules. For example, microcapsules with a red normal reflection showed blue cross-communication in a fluid with the same composition as the alignment layer; this reflection became green in air. This was also confirmed by the reflectance spectra shown in Figure 4e; the second peak is shifted from 458 nm to 536 nm. The change in color is caused by strong refraction at the air–membrane interface, which reduces the reflection angle in the CLC core from 45° to 34.2° (Figure S10b); the refractive index was estimated to be 1.424 from the second peak position by using ray tracing, indicating that the alignment shell still contains a small amount of water.

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The microcapsules retain the spherical shape without buckling during water evaporation owing to the thinness of the alignment layer.[30] The high structural and optical stability of the microcapsules in air enables the infiltration of an elastomer precursor into the interstices between the microcapsules and the formation of photonic films into which the CLC drops enclosed by alignment shells are embedded (Figure 4d,f,g); the elastic matrix is made of the same materials as the membrane. The photonic film shows blue cross-communication owing to insignificant refraction at the elastomer–alignment layer interface caused by the negligible difference in refractive index (Figure S10c). The reflectance spectrum recorded for the photonic film shows a second peak at 460 nm, which is coincident with that of microcapsules in the water and glycerol mixture.

The elastic deformation of the microcapsules and the adaptive molecular orientation potentially render the optical properties as well as the shape highly reconfigurable. This class of photonic ink capsules has great potential as new building blocks for the construction of photonic devices. For example, the microcapsules can be deformed and densely packed to form void-free panels. More importantly, the spontaneous rearrangement of CLC molecules guided by the alignment layer in each deformed microcapsule can maximize the reflection intensity of the panels. Furthermore, each microcapsule can serve as a stand-alone microsensor. For example, the microcapsules could be used as strain sensors when they are embedded in a flexible matrix as they display deformation-dependent reversible changes in the reflectivity. Temperature-dependent shifts in the structural colors of the CLCs render the microcapsules useful for injectable and dispersible colorimetric thermometers.[12] The photonic microcapsules, which are stable even in air, can be used for laser resonators. Although CLC droplet-based omnidirectional lasers have been implemented,[31] a liquid environment is prerequisite to maintain the spherical resonators, which severely restricts their use. Reconfigurable microcapsules will enable the control of the laser power through adjusting the deformation. Moreover, the laser direction can also be adjusted by controlling the deformation direction. We expect that a wide range of photonic applications beyond the above examples will benefit from these reconfigurable photonic microcapsules.

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