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Size Control of Cholesteric Liquid Crystalline Microcapsules

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We have succeeded the size-controlled fabrication of water-in-oil-in-water (W/O/W) double emulsion droplets with a cholesteric liquid crystalline (CLC) material, which is a mixture of a nematic liquid crystalline compound, 4-cyano-4′-pentylbiphenyl (5CB), and a chiral dopant, 1,4:3,6-dianhydro-2,5-bis[4-(n-hexyl-1-oxy)benzoic acid]sorbitol [ISO(6OBA)$_2$], as the shell phase and an aqueous poly(vinylalcohol) (PVA) solution as the core and outer phases (CLC microcapsules). Here we report the size-controlled fabrication of the CLC microcapsules and the size-dependence of their transmission spectra.

Keywords cholesteric liquid crystals; microfluidic devices; water-in-oil-in-water double emulsion; 4-cyano-4′-pentylbiphenyl; 1,4:3,6-dianhydro-2,5-bis[4-(n-hexyl-1-oxy)benzoic acid]sorbitol

Introduction

Cholesteric liquid crystalline (CLC) materials work as one-dimensional (1-D) photonic crystals with helical structure leading to periodic refractive indices. CLC materials inhibit the light propagation in a certain range of visible wavelengths, photonic band gap (PBG), which depends on temperature. Thus, the color of the selective reflection of CLC phase changes in heating and cooling process. The PBG enables 1-D, two-dimensional (2-D) and three-dimensional (3-D) laser action in well-aligned planar CLC materials [1], in CLC-filled optical fibers [2] and in CLC droplets in spite of the presence or absence of an aqueous droplet inside each CLC droplets, respectively [3, 4]. Since the CLC droplets show the selective reflection independent of the rotation at a fixed incident angle of the light, they work as temperature sensors [5]. Especially, the water-in-oil-in-water double emulsion CLC droplets (CLC microcapsules) hold great promise for the optical application because both hydrophilic and hydrophobic additives are utilizable; in fact, we have reported that CLC microcapsules with hydrophilic and hydrophobic dyes show one and two modes of laser actions, respectively [4]. In addition, we successfully fabricated the CLC microcapsules

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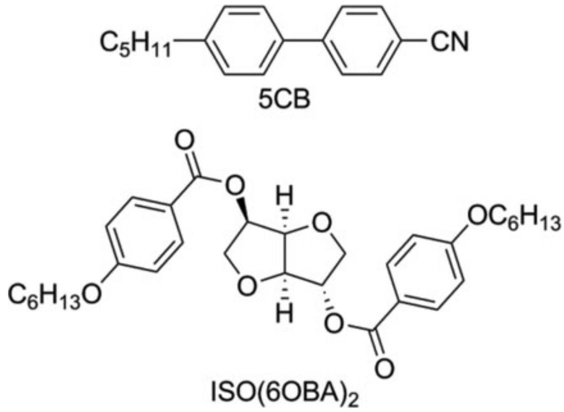

Figure 1. Molecular structures of 5CB and ISO(6OBA)$_2$.

containing an aqueous luminol solution as the core phase using a microfluidic device, which works as sensitive H_2O_2 sensors [6].

The PBG of well-aligned planar CLC materials, which is important for optical applications, is determined only by composition and operating temperature. However, as far as we know, the dependence of the PBG on the size of the CLC microcapsules is not clear. Here, we report the fabrication of CLC microcapsules with various sizes and the dependence of the transmission spectra on the size.

Experimental

Fabrication of CLC microcapsules

Unless otherwise noted, the outer and core phases were 10 wt% poly(vinyl alcohol) aqueous solution (PVA; MW: 13 000-23 000 g mol^{-1}, 87–89% hydrolyzed). For the CLC microcapsules, the shell phase was a mixture of a nematic liquid crystalline compound (4-cyano-4′-pentylbiphenyl [5CB]) and a synthesized chiral dopant (1,4:3,6-dianhydro-2,5-bis[4-(n-hexyl-1-oxy)benzoic acid]sorbitol [ISO(6OBA)$_2$], 5.0 wt%) (Fig. 1). The helical pitch of the CLC mixture is 352 nm at 21°C. W/O/W double emulsion droplets were fabricated using a glass microcapillary device [7]. The flow rates of the core and outer aqueous phases were kept constant at 0.7 and 11 mL h^{-1}, respectively. The size of the CLC microcapsule was controlled by the flow rates of the shell phase.

Measurement of transmission spectra of CLC microcapsules

2-D transmission spectra of the CLC microcapsules were measured using a 2-D imaging spectrometer (CLP-50: Bunkou Keiki) and an optical microscope (BX51: Olympus) at 25°C by using the experimental setup schematically illustrated in Fig. 2 [5].

Numerical simulation

For the numerical simulation of the transmission spectra by the Berreman method [8], we arranged a whole path such that the transmittance light is parallel to *z*-axis as shown in Fig. 3, cholesteric helical axes are perpendicular to the core and outer interfaces. As the

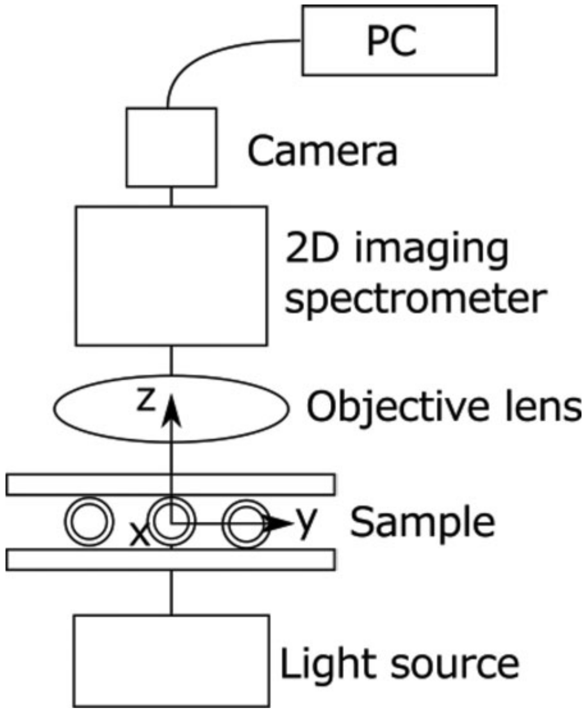

Figure 2. Experimental setup of 2-D transmission spectroscopy.

simulation of emission spectra in ref. [4], light refracted at the interfaces propagates straight both in aqueous and CLC phases for simplicity, though the periodic change of refractive indices affects the transmittance. We assumed that the refractive index of the aqueous core and outer phases was 1.34, and the refractive indices of the long and short axes of the CLC phase were 1.77 and 1.58, and the helical pitch of the CLC phase was 339 nm. We obtained the 2-D transmission spectra in a similar manner to that in ref. [4].

Results and Discussion

We prepared CLC microcapsules with various sizes using a microfluidic device [5]. The CLC material used was a mixture of 5CB and ISO(6OBA)$_2$. Core and outer aqueous phases of the emulsions were composed of 10 wt% aqueous PVA solution, which stabilizes the double emulsion and enforces tangentially aligning condition for CLC materials [9, 10]. The outer radius, R, of the double emulsions varied from 197 to 210 μm by changing the flow rate of the shell phase from 0.4 to 2.0 mL h^{-1}, while the core radius, a, varied from 179 to 153 μm (Fig. 4).

We measured the spatial dependence of transmission spectra of the CLC microcapsules with various sizes. The spectra were measured by using a 2-D imaging spectrometer and an optical microscope from the z direction of CLC microcapsules defined in Fig. 2. The system of coordinates with their origin at the center of the CLC microcapsules was adopted. Fig. 5 shows experimental and simulated 2-D profiles of spatially modulated spectra along the y direction at $x = 0$. Simulated spectra are qualitatively consistent with the corresponding experimental spectra. Thus, the 2-D profile suggests that the helical axes in the CLC

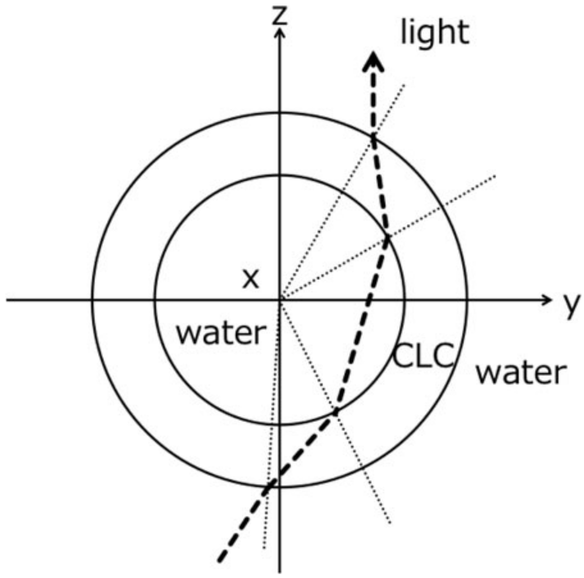

Figure 3. Configuration applied to the simulation. A whole path in *y-z* plane is arranged such that the transmittance light is parallel to *z*-axis. For simplicity, we assume light propagates straight both in aqueous and CLC phases.

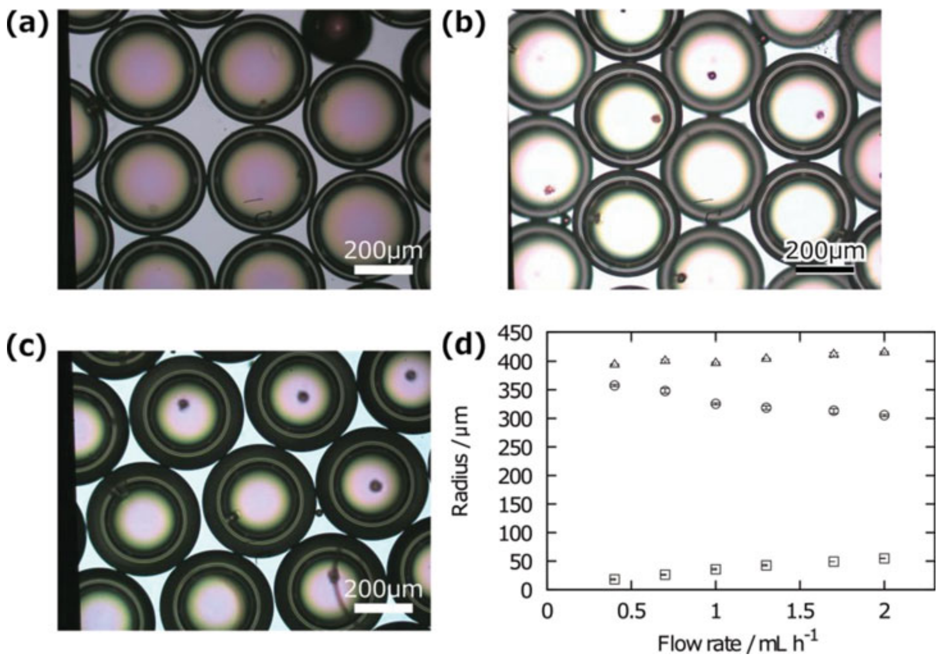

Figure 4. Dependence of the size of the CLC microcapsules on the flow rate of the shell phase. Bright-field microphotographs of the CLC microcapsules fabricated at the flow rate of the shell phase of (a) 0.4, (b) 1.0, and (c) 2.0 mL h^{-1}. (d) Plots of the diameter for core radius a (open circle), outer radius R (open triangle), and the thickness of the CLC shell $R - a$ (open square) as a function of the flow rate of the shell phase. These values are the mean values of three measurements at each flow rate.

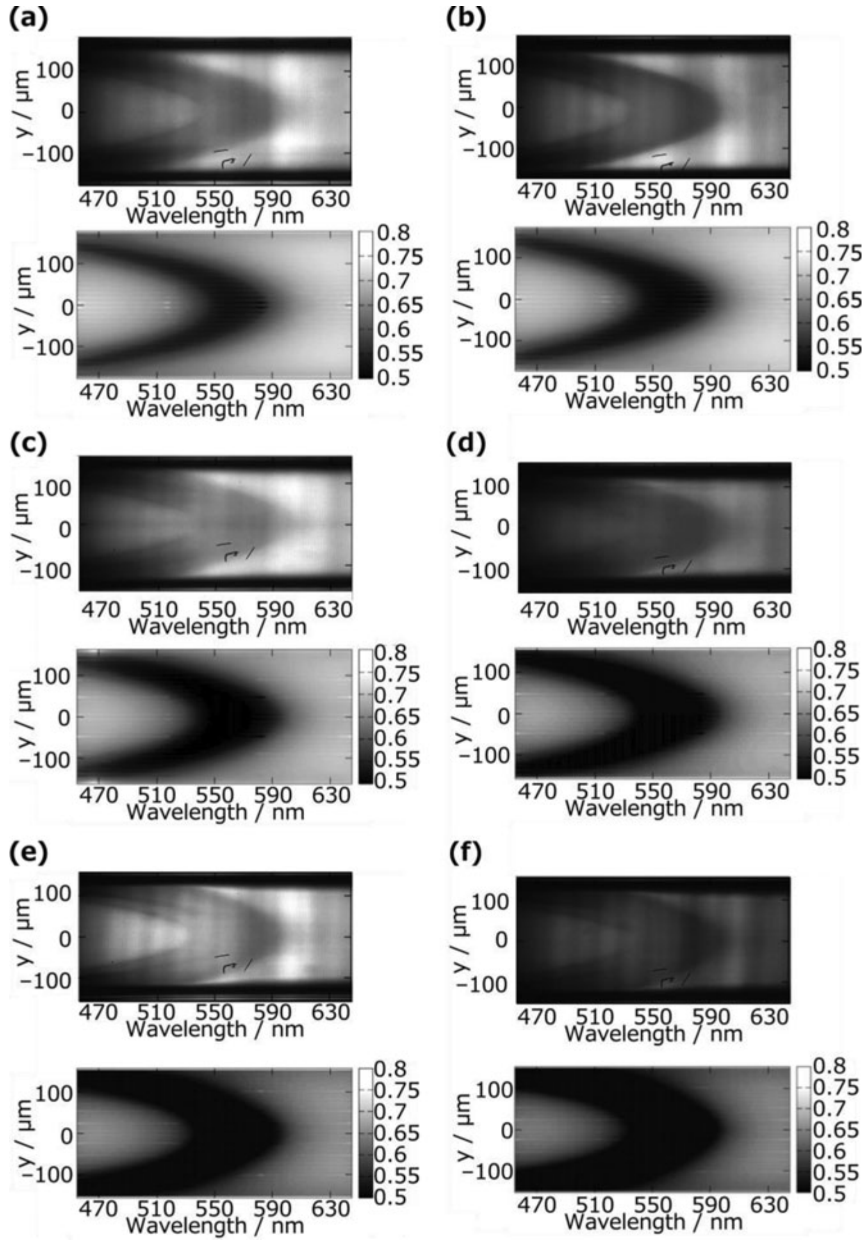

Figure 5. 2-D transmission spectra of CLC microcapsules for mapping of the spectra on the shell surface. Experimental (above) and simulated (below) 2-D transmission spectra of CLC microcapsules with (a) $(R, a) = (200\ \mu\text{m}, 179\ \mu\text{m})$, (b) with $(R, a) = (200\ \mu\text{m}, 174\ \mu\text{m})$, (c) with $(R, a) = (200\ \mu\text{m}, 163\ \mu\text{m})$, (d) with $(R, a) = (200\ \mu\text{m}, 159\ \mu\text{m})$, (e) with $(R, a) = (210\ \mu\text{m}, 157\ \mu\text{m})$, and (f) with $(R, a) = (210\ \mu\text{m}, 153\ \mu\text{m})$.

microcapsules are likely to be arranged in a radial fashion as reported in refs. 4 and 5. In addition, the PBG depends on the shell thickness; the width of PBG increases at $y \neq 0$ as the shell thickness increases.

Conclusion

We have succeeded the size-controlled fabrication of CLC microcapsules with a CLC mixture consisting of 5CB and ISO(6OBA)$_2$ as the shell phase and the simulation of the 2-D transmission spectra of the CLC microcapsules, and found that they show the dependence of PBG on the shell thickness. This indicates that the size control of the CLC microcapsules is very important for optics application: lasers and sensors.

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