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Temperature-dependent Color Change of Cholesteric Liquid Crystalline Core-shell Microspheres

(**Cholesteric LC Core-shell Microspheres** for running head**)**

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Abstract

We have fabricated 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, cholesteryl oleyl carbonate (COC), as the middle phase and an aqueous poly(vinylalcohol) (PVA) solution as the inner and outer phases (CLC core-shell microspheres). Here we report the strongly temperature-dependent color change of CLC core-shell microsphere.

Keywords: cholesteric liquid crystals; microfluidic devices; water-in-oil-in-water double emulsion; 4-cyano-4'-pentylbiphenyl; cholesteyl oleyl carbonate

INTRODUCTION

Cholesteric liquid crystalline (CLC) phases have periodic helical structured refractive indices and operate as one-dimensional (1-D) photonic crystals. CLC materials inhibit the emission of the dye dissolved in the CLC materials themselves in a certain range of visible wavelengths, photonic band gap (PBG), and instead, they enhance the emission at the band edges. Since PBGs of CLC materials depend on temperature,[1] their colors change with temperature change. Temperature-dependent 1-D lasing in planar aligned CLC materials was reported.[2] Furthermore, temperature-dependent 3-D omnidirectional lasing in tangential aligned CLC droplets was also reported.[3] PBGs of the CLC droplets are independent of the rotation under illumination of the surface at a fixed incident angle of the light. Thus, CLC droplets could work as temperature sensors. We have recently reported an omnidirectional laser action based on CLC core-shell microspheres, which are water-in-oil-in-water (W/O/W) double emulsion droplets containing a CLC phase as the middle phase.[4] The CLC core-shell microspheres hold great promise for the optical application because both hydrophilic and hydrophobic dyes are utilizable as the laser dye. Since colors of the CLC core-shell microspheres should depend on temperature, they could also work as temperature sensors.

Here, we report the fabrication and the temperature-dependent color change of novel CLC core-shell microspheres, whose PBG more strongly depends on temperature than that of the previously reported CLC core-shell microspheres.

EXPERIMENTAL

Fabrication of CLC core-shell microspheres

To obtain the CLC core-shell microspheres consisting of an aqueous PVA (PVA; Mw: 13000–23000 g mol^{-1}, 87–89% hydrolyzed) solution as the inner and outer phases and a CLC material as the middle phase, we employed the microfluidic device (**Fig. 1a, 1b**). The CLC material used was a mixture of a nematic liquid crystalline compound (4-cyano-4’-pentylbiphenyl (5CB)) and a chiral dopant (cholesteryl oleyl carbonate (COC)). PVA stabilizes the structure (**Fig. 2a**) and enforces tangential alignment of the CLC materials (**Fig. 2b**). The outer diameter and shell thickness of the CLC core-shell microcapsules obtained were about 350 μm and 30 μm, respectively (**Fig. 2c**).

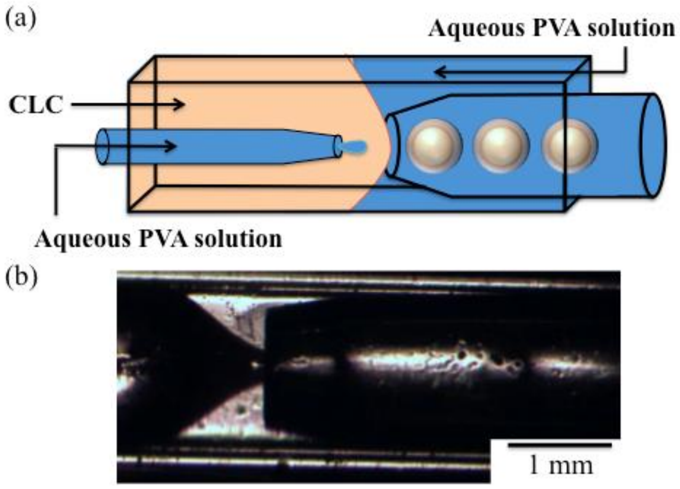

Fig. 1 Schematic of the microcapillary geometry for generating CLC core-shell microspheres. (a) The geometry required the outer phase to be immiscible with the middle phase, which is in turn immiscible with the inner phase. (b) Optical micrograph of the microfluidic device.

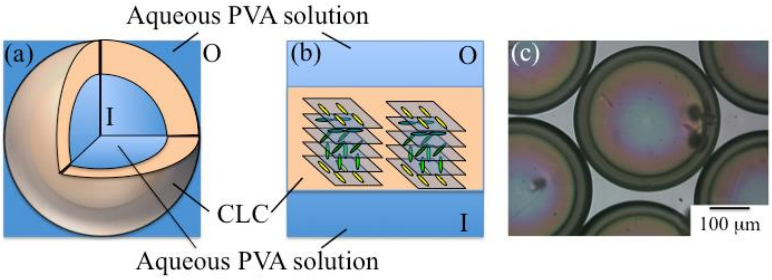

Fig. 2 Schematic of the structure of CLC core-shell microspheres. (a) The water-in-oil-in-water (W/O/W) emulsion droplets have inner and outer aqueous phases and a middle CLC phase. I and O denote inner and outer phases, respectively. (b) The helical axes in the CLC phase are perpendicular to the interface. (c) Bright-field microphotograph of the CLC core-shell microspheres.

Measurement of transmittance spectra of CLC core-shell microspheres

Two-dimensional (2-D) transmittance spectra of the CLC core-shell microspheres were measured using a two-dimensional imaging spectrograph (CLP-50: Bunkou Keiki) and an optical microscope (BX51: Olympus). The system is schematically illustrated in **Fig. 3a**. Furthermore, we measured the temparature dependence of the PBGs of CLC core-shell microspheres from 26°C to 36°C in the heating run.

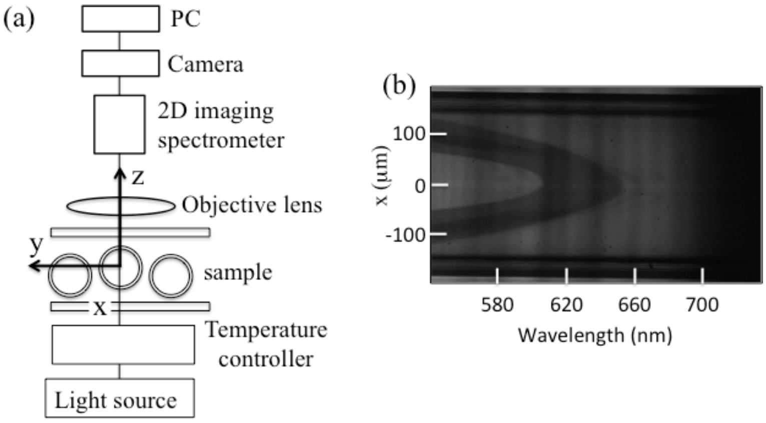

Fig. 3 Two-dimensional (2-D) transmittance spectra of a CLC core-shell microsphere for mapping of the spectra on the shell surface. (a) Experimental setup of the 2-D transmittance spectroscopy. (b) 2-D transmittance spectra of a CLC core-shell microsphere with the outer diameter of 353 μm and shell thickness of 31 μm.

RESULTS AND DISCUSSION

We prepared CLC core-shell microspheres using a microfluidic device (Fig. 1a, 1b).[5] The resultant double-emulsion droplets consist of an inner aqueous droplet, encapsulated within a CLC shell, and they are immersed in an aqueous solution (Fig. 2a). The CLC material used was a mixture of 5CB and COC and showed a PBG between 543 nm and 583 nm at 26°C. Inner and outer aqueous phases of the emulsions are composed of 10 wt% aqueous PVA solution, which stabilizes the double emulsion and enforces tangentially aligning condition for CLC materials (Fig. 2b).[6, 7] The outer diameter and shell thickness of the CLC core-shell microsphere were about 353 μm and 31 μm, respectively (**Fig. 2c**).

We measured the spatial dependence of transmittance spectra of the CLC core-shell microspheres. The experimental setup is schematically illustrated in Fig. 3a. Using a two-dimensional (2-D) imaging spectrograph and an optical microscope, spectra were measured from the z direction of CLC core-shell microspheres defined in Fig. 3a. We adopted the system of coordinates with their origin at the center of the CLC core-shell microspheres. **Fig. 3b** shows a 2-D profile of spatially modulated spectra along the x direction at $y = 0$, and the PBG depends on the position. The 2-D profile suggests that the helical axes in the CLC core-shell microspheres are likely to be arranged in a radial fashion as reported in reference 4.

Furthermore, the PBGs of CLC core-shell microspheres were blue-shifted with increasing temperature from 26°C to 36°C, as opposed to those of the previously reported CLC core-shell microspheres with a CLC mixture consisting of ZLI-2293 and MLC-6248 (Merck), which were red-shifted with increasing temperature.[4] It is well-known that although the PBGs of most CLC mixtures are blue-shifted with increasing temperature, there are some exceptions.[8] The decreasing rate of the PBG was 3.3 nm/K (**Fig. 4**). This decreasing rate is larger than the increasing rate of the previously reported CLC core-shell microspheres (ca. 1 nm/K).[4] In the room temperature range, the photonic structures of the CLC core-shell microspheres are likely to be stable.

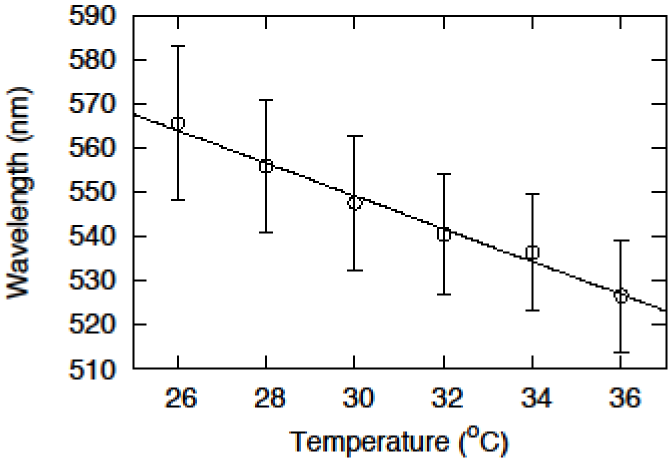

Fig. 4 Temperature dependence of the center of the PBG of the CLC core-shell microspheres at $x = y = 0$. Error bars denote the width of the PBG at each temperature.

CONCLUSION

We have successfully fabricated CLC core-shell microspheres with a CLC mixture consisting of 5CB and COC as the middle phase, and found that they show strongly temperature-dependent color change. The CLC core-shell microspheres were stable in the room temperature range where the CLC phase is stable, and thus they may be promising materials for temperature sensors in the room temperature range.

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