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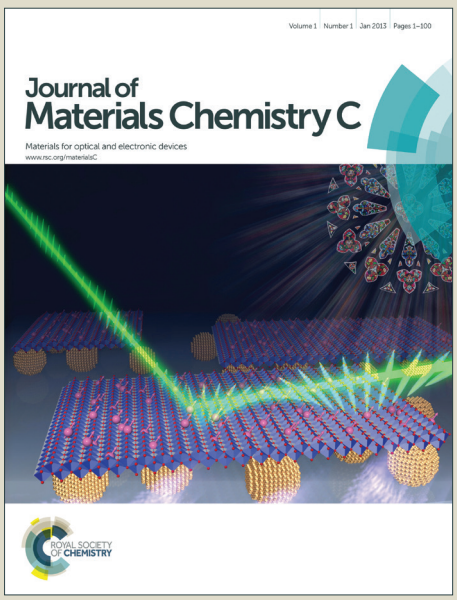

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Chemiluminescence Emission in Cholesteric Liquid Crystalline Core-shell Microcapsules

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Chemiluminescence behaviour in the core region of water/oil/water double emulsion droplets with cholesteric liquid crystalline (CLC) middle phase (CLC core-shell microcapsules) was demonstrated. We successfully fabricated CLC core-shell microcapsules containing an aqueous luminol solution as the inner phase using a microfluidic device, in which the helical axis of the CLC phase is normal to the surface. The CLC core-shell microcapsules proved to be a plausible candidate for highly sensitive H_2O_2 sensors because of the omnidirectional photonic structures of the CLC phase.

Introduction

Chemical sensors can detect the presence and quantity of various substances: conjugated polymers[1] and graphene[2] can act as metal ion sensors; carbon nanotubes[3,4] can be used to detect O_2, NO_2 and NH_3; and ZnO nanoparticles and nanorods[5] have been used to detect formaldehyde and xylene. Sensors operating through chemiluminescence are one of the most effective types of chemical sensors, often exhibiting high sensitivity and signal-to-noise ratios. The luminol reaction, in particular, is one of the most commonly used chemiluminescence reactions, where H_2O_2 oxidizes luminol in the presence of catalytic metal ions such as Fe^{3+}, Cu^{2+} and Co^{2+}. The luminol reaction is promising for applications in forensic tests for blood[6] and in biochemical assays to detect H_2O_2 as a marker of inflammation.[7]

Biochemical assays and immunoassays on a chip require carriers to restrict reaction fields to within a small space. Single and double emulsion droplets formed by immiscible aqueous and oil surfactant solutions and liposomes in which an aqueous phase is enclosed by lipid bilayer can be used to encapsulate materials and drugs for assays. The encapsulation of chemiluminescent molecules in liposomes has been reported.[8] For application in nano- or micro-sized microfluidic sensors, the chemiluminescence reactions must have high sensitivity. To improve the limits of detection of the microfluidic sensors, optimization of the luminol reaction conditions has been explored, including the development of better-performing luminol derivatives;[9] the choice of metal complexes as a catalyst;[10,11] reaction temperature and pH.[12] Another way to improve the limits of detection of microfluidic sensors is to increase the amount of measurable luminescence using photonic structures. In photonic structures the emission of the dye is restricted to a certain range of visible wavelengths known as photonic band gap (PBG), and the emission intensity at the PBG edges is enhanced. Although chemiluminescence emission is also expected to be affected by photonic structures, such effects have not been reported.

Cholesteric liquid crystalline (CLC) phases have periodic helical structured refractive indices and operate as one-dimensional photonic crystals. Enhancement of the emission of dyes dissolved in CLC materials has been found to occur, and lasing has been observed in planar aligned CLC materials doped with an appropriate dye.[13] Moreover, the molecular alignment of the CLC phases depends on the boundary conditions at the interface and on the shape of the interface. The simple case of a director field in the CLC droplet with tangential alignment conditions has been well studied theoretically and experimentally.[14] The CLC droplets have the radial arrangement of the helical axes, such that the structures perform as omnidirectional laser resonators.[15] We have recently reported an omnidirectional laser action based on CLC core-shell microcapsules, which are water/oil/water (W/O/W) double emulsion droplets containing a CLC phase.[16] This structure not only operated as an omnidirectional laser resonator but could also be used to encapsulate chemicals. Using the CLC core-shell microcapsule it should be possible to enhance chemiluminescence emission in three dimensions.

Here, we report the emission behaviour of a luminol reaction restricted to the core region of the CLC core-shell microcapsules. This is the first example of chemiluminescence reaction in ominidirectional photonic structure. First, to examine whether the PBG of the CLC phases enhances the maximum chemiluminescence emission intensity of the luminol reaction, we measured the emission

spectra of the luminol reaction in a cell sandwiched between two planar CLC reflectors with cholesteric helical axis perpendicular to the cell plane. Next, we prepared CLC core-shell microcapsules consisting of an aqueous luminol solution as the inner phase and a CLC material as the middle phase using a microfluidic device. Finally, we examined whether the chemiluminescence emission intensity in the core region of the CLC core-shell microcapsules increases.

Results and discussion

Effects of CLC reflectors on maximum emission intensity of luminol reaction

To confirm whether the one-dimensional PBG enhances the intensity of the emission spectra maximum of the luminol reaction, we prepared planar CLC reflectors between two treated glass plates (see Experimental section), in which the helical axes of the CLC materials were perpendicular to the cell planes (Figure 1a). It is well-known that when the PBG edge is near the emission peak, the luminescent enhancement is most effective. Therefore, we prepared two CLC mixtures of ZLI-2293 (Merck) and MLC-6248 (Merck). On the one hand, CLC mixture **1** shows a PBG between 2.69 eV (461 nm) and 2.90 eV (428 nm) in the transmittance spectra at 26 °C (Figure 1b, S1(a), see Experimental section): the lower PBG edge (428 nm) is near the emission peak of the luminol reaction.[16] On the other hand, CLC mixture **2** shows a PBG between 2.89 eV (429 nm) and 3.12 eV (397 nm) in the transmittance spectra at 26 °C (Figure S1(b)): the higher PBG edge (429 nm) is near the emission peak of the luminol reaction.[16] The CLC reflectors exhibited blue or purple, temperature dependent colour indicating selective reflection of light with wavelengths corresponding to the PBG (Figure 1c, S2).

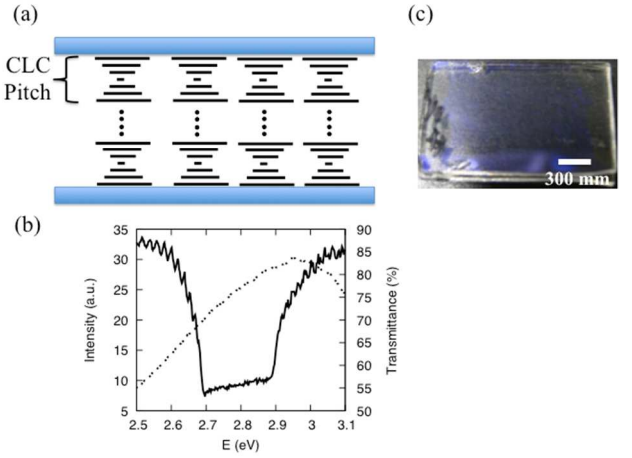

Figure 1. Transmittance spectra of a cholesteric liquid crystalline (CLC) reflector. (a) Schematic of CLC reflector. The helical axes in the CLC phase are perpendicular to the glass surface. (b) Emission spectra of luminol (broken line) and transmittance spectra of the CLC reflector of the mixture **1** (solid line). (c) Photograph of the CLC reflector of the mixture **1** showing Bragg reflection colour.

A plastic cell filled with an aqueous luminol solution containing Cu^{2+} ions was sandwiched between two planar CLC reflectors. We used an alkaline buffer solution as the luminol solution to enhance the emission intensity of the luminol reaction. We added an H_2O_2 solution to the aqueous luminol solution in the plastic cell and measured the emission spectra perpendicular to the reflector plane using a spectrofluorometer (Figure 2a, see Experimental section).

The emission intensity in the PBG of the CLC material is depressed compared with the emission spectra measured without the reflectors (Figure 2b, S3). The emission spectra of the sample with the reflectors showed a higher maximum intensity at the PBG edge than the sample without the reflectors. The peak intensity of the emission spectra using the CLC reflector of the mixture **1** is higher than that of the mixture **2**. Thus, we used only the mixture **1** to prepare reflectors and microcapsules (Figure S4). The integral from 2.84 eV (436 nm) to 3.08 eV (403 nm) of the emission spectrum of the sample with the reflectors of the mixture **1** is 1.06 times larger than that of the sample without the reflectors. These results indicate that the reflectors inhibit the chemiluminescence emission of the luminol reaction in the PBG, and instead enhance the emission around the PBG edges such that the maximum emission intensity increases. Thus, we can conclude that the planar CLC reflectors raise chemiluminescence emission maximum of luminol reaction.

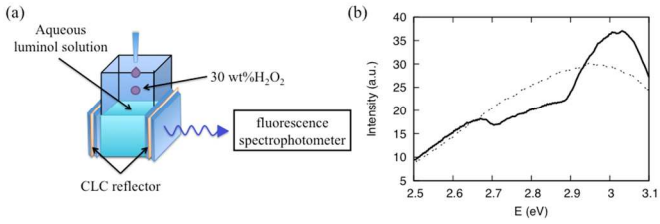

Figure 2. The effects of CLC reflectors on luminol emission. (a) Experimental setup of luminol emission spectra measurement. (b) Emission spectra (Intensity vs. Energy (E)) of luminol with the CLC reflectors (solid line) and without the reflectors (broken line).

Effects of CLC core-shell microcapsules on maximum emission intensity of luminol reaction

Next, we prepared CLC core-shell microcapsules consisting of a CLC material as the middle phase, an aqueous luminol solution as the inner phase and an aqueous poly(vinyl alcohol) (PVA) solution as the outer phase, using microfluidic devices (see Experimental section).[18] PVA stabilizes the double emulsion and enforces tangential alignment of the CLC materials (Figure 3a).[19,20] We used an alkaline buffer solution as the inner phase to enhance the emission intensity of the luminol reaction, whereas a neutral buffer solution was used as the outer phase to avoid luminol reactions occurring in the outer phase. The outer diameter (D) and shell thickness (d) of the CLC core-shell microcapsules obtained were several hundreds and several tens of μm, respectively (Figure 3b).

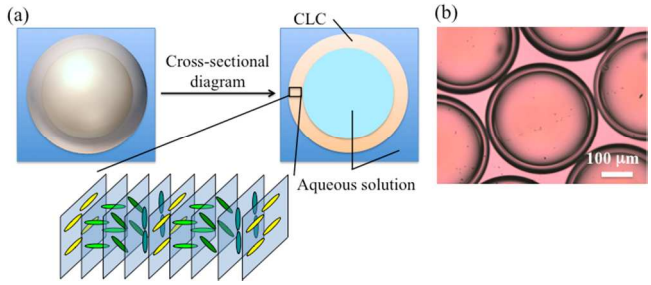

Figure 3. Structure of CLC core-shell microcapsule. (a) The water/oil/water emulsion has inner and outer aqueous phases and a middle CLC phase. The helical axes in the CLC phase are perpendicular to the interface. (b) Bright-field microphotograph of the CLC core-shell microcapsules.

We added an H_2O_2 solution to the outer phase of the CLC core-shell microcapsules (D = 341 μm, d = 25 μm) containing the luminol

solution, and then, measured the time-dependent emission intensity using a photomultiplier tube. Although emission spectra of the luminol reaction in one core-shell microcapsule should be measured to ascertain the effect of the PBG of the CLC material on the chemiluminescence emission in the inner phase, the emission intensity per core-shell microcapsule is too weak to measure the spectra. Thus, we measured the integrated emission intensity from 2.84 eV (436 nm) to 3.08 eV (403 nm) using a cut off filter (see Experimental section); this range includes both the peak wavelengths of the emission spectra of the luminol reaction measured with and without CLC reflectors (Figure S2). The experimental setup is schematically illustrated in Figure 4a. The emission intensity increased linearly for the first 50 seconds, and then decreased. These results indicate that H_2O_2 permeated the core of the CLC core-shell microcapsules and the luminol reaction started to occur (Figure 4b).

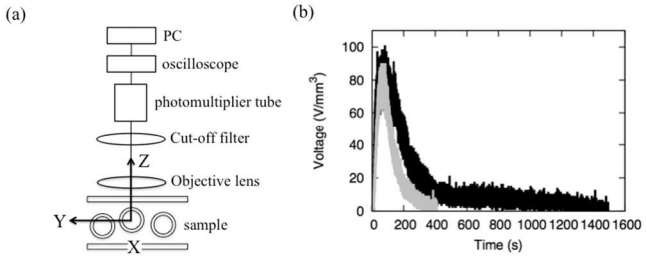

Figure 4. Emission intensity of the luminol reaction in the CLC and NLC core-shell microcapsules. (a) Experimental setup for the emission intensity measurement of the luminol reaction in the CLC and NLC core-shell microcapsules. (b) Black line is the emission intensity of the luminol reaction in the CLC core-shell microcapsules and grey line is that in the NLC core-shell microcapsules.

Then, the intensity decreased as the luminol in the core region was consumed. The rate at which the emission intensity increased could be controlled by changing the thickness of the middle phase of the core-shell microcapsules.

We also prepared nematic liquid crystalline (NLC) core-shell microcapsules, in which the middle phase was composed of an NLC material instead of a CLC material, for comparison. The NLC material used was a well-known compound, 4-cyano-4'-pentylbiphenyl (5CB), which does not show a PBG and exhibited different H_2O_2 permeation behaviour into the shell region. Permeation rate of H_2O_2 in 5CB is higher than that in the CLC mixture **1**. Thus, if the NLC and CLC core-shell microcapsules have the same thickness of the middle phases, the peak time of emission of the former is earlier than that of the latter. To compare the chemiluminescence emission with that in the CLC core-shell microcapsule, we adjusted the thickness of the middle phase of the NLC core-shell microcapsule to obtain the same delivery rate of H_2O_2 to the inner phase as that in the CLC core-shell microcapsule. This resulted in the middle phase of the NLC core-shell microcapsule (D = 430 μm, d = 45 μm) being 1.8 times thicker than that of the CLC core-shell microcapsules because the NLC phase showed higher rate of diffusion of H_2O_2 than the CLC phase.

After the addition of H_2O_2 solution, the emission intensity increased linearly for the first 50 seconds, before decreasing as was the case with the CLC core-shell microcapsules (Figure 4b). However, the emission intensities measured for the luminol reaction in the NLC core-shell microcapsules were lower than those of the CLC core-shell microcapsules (Figure 4b). The maximum emission intensity for the CLC core-shell microcapsules was 101 V mm^{-3} and 1.12 times higher than that for the NLC core-shell microcapsules (90 V mm^{-3}).

There are two possible reasons to induce the difference in the emission intensity between luminol reactions in the CLC and NLC core-shell microcapsules. One is the difference in light transmittance of the middle phases, and the other is the PBG of the CLC. The thickness of the middle phase of the NLC core-shell microcapsules is thicker than that of the CLC core-shell microcapsules. However, light transmittance of unit thickness for the NLC materials is enough higher than that for the CLC material (Figure S5). Therefore, the difference in the thickness of the middle phase does not account for the difference in the emission intensity. This implies that the PBG of the CLC enhances the chemiluminescence emission intensity in the core region, and therefore, the maximum emission intensity for the CLC core-shell microcapsules became higher than that for the NLC core-shell microcapsules. We can conclude that the CLC core-shell microcapsule improves the limit of detection of the H_2O_2 sensor. These results are consistent with the results of the emission spectroscopy for the luminol reaction in CLC reflectors.

Conclusions

We successfully fabricated for the first time CLC core-shell microcapsules using microfluidic devices that contained an aqueous luminol solution inner phase encompassed by a CLC material featuring a helical axis normal to the droplet surface as the middle phase. Consequently, the emulsion system of dispersed CLC core-shell microcapsules can increase the amount of measurable luminescence in the core region to effectively detect H_2O_2. Although this effect is not enough large now, there are some ways of further enhancement of the effect: introduction of a dye that enables the fast emission and narrow emission spectra, utilization of another CLC materials or colloidal crystals[21] with more wide PBG as the middle phase, fabrication of water/oil/water/oil/water emulsion[18b] with both right- and left-handed CLC materials.

As the centre of the core-shell structure is not composed of a CLC phase but of an isotropic aqueous phase, the CLC helical axis remains perpendicular to the shell surfaces even if the core-shell microcapsules become deformed. The PBG can be fine-tuned by the composition ratio of the NLC materials and the chiral dopants. Furthermore, this method could be extended to a variety of other chemiluminescent substances. Core-shell emulsion droplets hold great promise for applications of CLC materials to chemiluminescence sensors.

Experimental section

Fabrication of CLC reflector

1 wt% PVA aqueous solution (PVA; Mw: 1500 g mol^{-1}) was spin-coated onto glass substrates. Spin conditions were 4000 rpm for 30 s. After spin coating, the PVA-coated glass substrates were heated at 150^{o}C for 1 h to remove residual H_2O. After heating, the glass substrates were taken from the oven, and cooled to room temperature in a desiccator. All glass substrates were rubbed with velvet cloth five times. The cells were assembled so that the rubbing directions on the top and bottom planes were opposite (antiparallel configuration). The cells were filled with a CLC mixture consisting of a nematic liquid crystalline mixture (ZLI-2293: Merck) and a chiral dopant (MLC-6248: Merck) by capillary action.

Measurement of Transmittance spectra and emission spectra

Transmittance spectroscopy was carried out on an optical microscope (BX51: Olympus). The transmittance spectra were measured with a spectrometer (USB2000+UV-VIS: Optosirius). We pasted the CLC reflectors on two opposite sides of a plastic cell

containing a luminol aqueous solution. 9.1×10^{-2} wt% luminol and 4.1×10^{-2} wt% $CuSO_4\bullet5H_2O$ were dissolved in 8.4 wt% PVA (Mw: 13000–23000 g mol^{-1}, 87–89% hydrolyzed) aqueous solution (a carbonate-bicarbonate buffer solution; pH 10), 20 μl of 30 wt% H_2O_2 aqueous solution was added to 1 ml of the luminol aqueous solution and we measured the emission spectra of luminol reaction through the cell. The emission spectra were measured with a spectrofluorometer (FP-6500: Jasco) and fluorescence microplate reader (FMP-965: Jasco).

Fabrication of CLC core-shell microcapsules

W/O/W double emulsion droplets were produced using glass microcapillary devices.[18a] The outer radius and the inner radius were controlled by the size of the capillaries used and the flow rates of the different phases. The inner phase was 9.1×10^{-2} wt% luminol and 4.1×10^{-2} wt% $CuSO_4\bullet5H_2O$ dissolved in an 8.4 wt% PVA aqueous solution (PVA; Mw: 13000–23000 g mol^{-1}, 87–89% hydrolyzed), and the outer phase was a 9.9 wt% PVA aqueous solution. We employed a carbonate-bicarbonate buffer solution (pH 10) as the inner phase, whereas we employed a phosphate buffer solution (pH 7) as the outer phase. For CLC core-shell microcapsules, the middle phase is the same CLC as using for the above-mentioned CLC reflectors, and had the same right-handed helicity. For NLC core-shell microcapsules, the middle phase is 4-cyano-4'-pentylbiphenyl.

Measurement of Time-dependent emission intensity

For the measurement of emission intensity 15 wt% H_2O_2 aqueous solution was added to the outer aqueous phase of the CLC or NLC core-shell microcapsules. Time-dependent emission intensity was measured using a photosensor module (H10721-210: Hamamatsu Photonics) with power supply for PMT module (C10709) and a digital oscilloscope (LT-344 500MHz: Iwatsu-Lecroy) attached to an optical microscope (BX51: Olympus). To measure the emission intensity between 2.84 eV (436 nm) and 3.08 eV (403 nm), we used the cut off filter (YIF-BP400-440S: SIGMA KOKI).

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Notes and references

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