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IN-SITU OPTICAL MONITORING OF LANGMUIR-BLODGETT FILMS DEPOSITED ON OPTICAL FIBERS

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Abstract Absorption spectra of adsorption Langmuir-Blodgett (LB) films were measured during and after the deposition of malachite green adsorbed merocyanine LB films on an optical fiber. The experimental results show that the in-situ optical monitoring using optical fibers is one of the powerful method to investigate the optical properties and the molecular interactions in the adsorption LB films.

INTRODUCTION

The adsorption Langmuir-Blodgett (LB) technique[1-5] makes it possible to fabricate LB films containing functional molecules using molecular interaction. It is one of the expecting method for the realization of molecular electronic devices. The authors reported the molecular interaction between triphenylmethane (TPM) dyes and merocyanine dyes (MC) in LB films prepared by this technique.[4-6] However, the adsorption LB films containing organic dye, protein, and bio-materials, often show an instability after the film fabrication. Thus, in-situ monitoring during the deposition is important to investigate the optical properties and molecular interactions in LB films, such as nonlinear optics, molecular adsorption, charge-transfer complex formation, etc.

In this report, we employed merocyanine derivative having a long alkyl chain (C_{18}MC) and malachite green (MG) molecules as spreading and adsorbing materials, respectively. The adsorption LB films were directly deposited on optical fibers. Absorption spectra due to the optical interaction with the LB film at the stripped core portion of the optical fiber were monitored during the deposition. Furthermore, this experimental method is attractive because it permits the excitation of specific molecules and monitoring the adsorption and fluorescent spectra.

EXPERIMENTAL

In fabricating the adsorption LB films, C_{18}MC was used as spreading material for

monolayers on the subphase and MG that belongs to TPM dyes was used as the adsorbing material to $C_{18}MC$ monolayers from the subphase. The chemical structures of these materials are shown in Figure 1. It is known that MC has p-type and MG has n-type properties.[7] The MG adsorbed $C_{18}MC$ LB films have a Y-type structure.

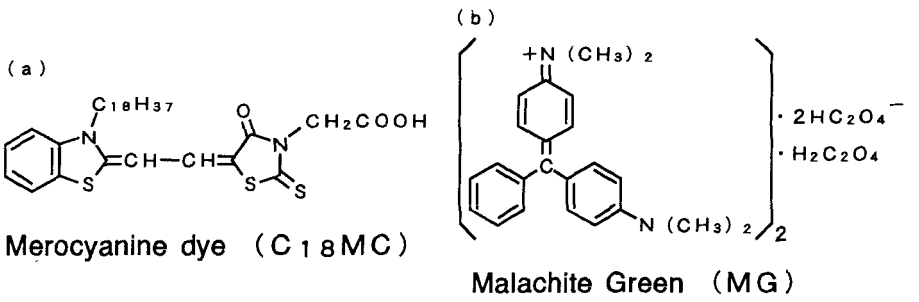

FIGURE 1 Chemical structure of using materials.
(a) merocyanine ($C_{18}MC$), (b) malachite green (MG)

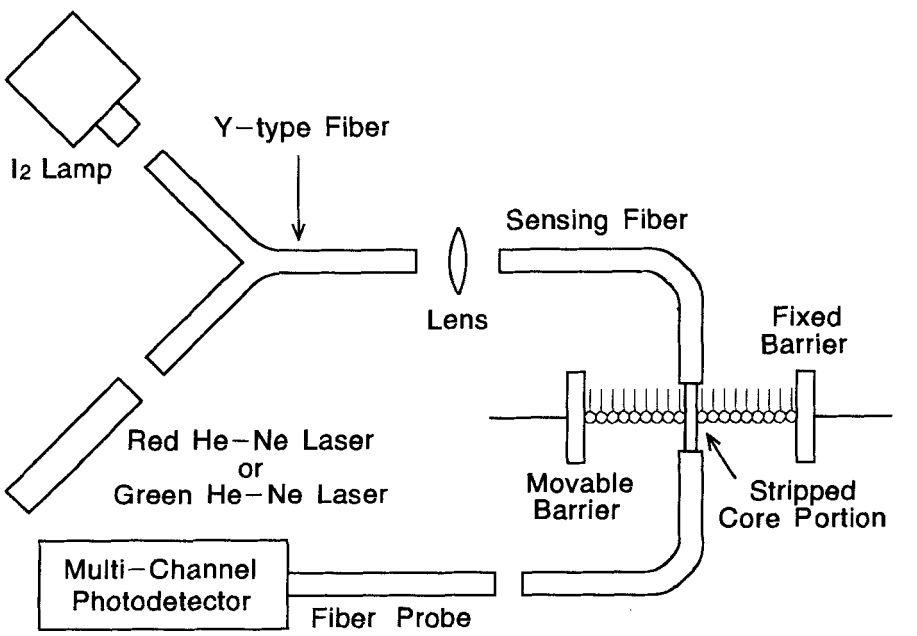

FIGURE 2 Schematic diagram of the experimental system.

A schematic diagram of the experimental system is shown in Figure 2, consisting of a red He-Ne laser (632.8nm) for MG excitation, a green He-Ne laser (543.5nm) for MC excitation, an I_2 lamp for spectra measurement, a light incident Y-type fiber, a sensing fiber for LB deposition, multi-channel photodetector with a fiber optic probe, and an LB trough. The Y-type fiber was used to guide the light from the I_2 lamp into the sensing fiber to obtain the absorption spectra and that was also used to guide the 632.8nm light or 543.5nm light into the sensing fiber for MG and MC excitation, respectively. The core and clad materials of the sensing fiber were made of quartz and polyimide, respectively. The diameter of the fiber core was about 100μm. The covered and clad layers of about 1.5cm long of the sensing fiber were mechanically stripped from the center of the fiber. Onto the stripped fiber core portion, LB films were directly deposited. The incident light interacted with molecules at the core portion and that was coupled into the fiber optic probe. Spectra were collected over a range 400-800nm by the multi-channel photodetector.

The experimental procedure was as follows. First, a monolayer of C_{18}MC was formed onto the subphase of deionized-distilled water or water containing $4x10^{-4}$M $CdCl_2$, $5x10^{-5}$M $KHCO_3$, and $3x10^{-5}$M MG. The pH value of the subphase was 5.8-6.2. Second, the monolayer was compressed to a surface pressure of 20mN/m. Third, the dipping started with a downstroke movement. The dipper was paused at the apexes of the upstrokes and downstrokes and absorption spectra of the deposited LB films at the core portion were collected at each stop.

In this study, the LB films were fabricated under three conditions. The first condition, no laser light was coupled into the Y-type fiber during the deposition. The second condition, only the 543.5nm light for MC excitation was coupled into the Y-type fiber. The third condition, only the 632.8nm light for MG excitation was coupled into the Y-type fiber.

RESULTS AND DISCUSSION

1. C_{18}MC LB films

Figure 3 shows the series of absorption spectra of C_{18}MC LB films deposited onto the optical fiber with no excitation light. It is known that MC LB films have three peaks that are a monomer-band at 540nm, a dimer-band at 500nm, and a J-band at 590nm in visible absorption spectra. In Figure 3, the absorption peak around 590nm that corresponds to J-aggregate of MC is clearly appeared, and the monomer-band and dimer-band are also observed in the spectra. The spectra measured in the subphase and air are shown in Figure 3(a) and (b), respectively. The difference of the absorption intensity

between the spectra measured in the subphase and air is due to the difference of the refractive indexes of the subphase (n=1.333) and air (n=1.000).[8] After the first down-stroke (no LB film deposition in Y-type structure), J-band was slightly appeared in Figure 3(a). This result should be caused by the slight deposition of C_{18}MC onto the fiber or the absorption weakly coupled with the C_{18}MC monolayer on the subphase. These results indicate that the in-situ monitoring using optical fibers has high sensitivity and that can evaluate thin films of less than one monolayer.

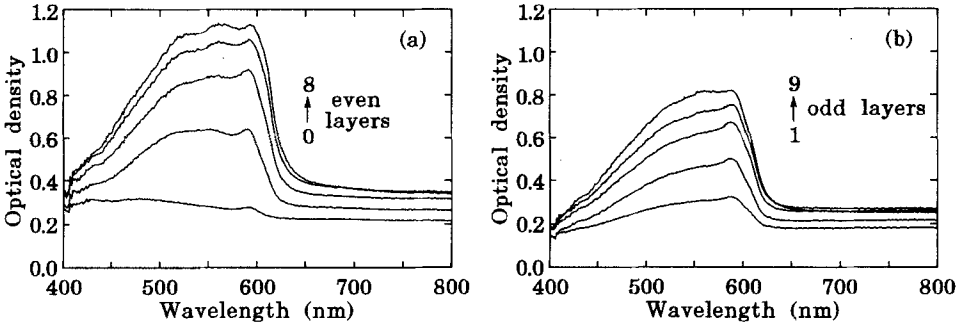

FIGURE 3 Absorption spectra of C_{18}MC LB films measured (a) in the subphase and (b) in the air. The number in the figure indicates the number of LB layers deposited.

2. MG adsorbed C_{18}MC LB films

The absorption spectra of MG adsorbed C_{18}MC LB films deposited onto the optical fiber are shown in Figure 4(a)-(d). All the spectra are measured in the air. MG has two absorption peaks around 430nm (Y-band) and 620nm (X-band).[9] The X-band and Y-band of MG are observed around 660nm and 440nm, respectively, and the J-band of C_{18}MC is observed around 600nm. These peaks show red-shift from their natural peak positions and those red-shift are remarkable as the number of the LB layers increases. These results might be related to the molecular interaction between C_{18}MC and MG.

Figure 4(a) and (b) show the absorption spectra of the adsorption LB films deposited with no excitation light and with the 632.8nm light for MG excitation, respectively. Comparing Figure 4(a) and (b), no remarkable difference is observed. However, when the excitation light was coupled into the fiber for 90 minutes after the 9 layers deposition, the absorption intensity was decreased all over the measurement range as shown in Figure 4(c). In particular, MG peaks show the large decrease. This result indicates that

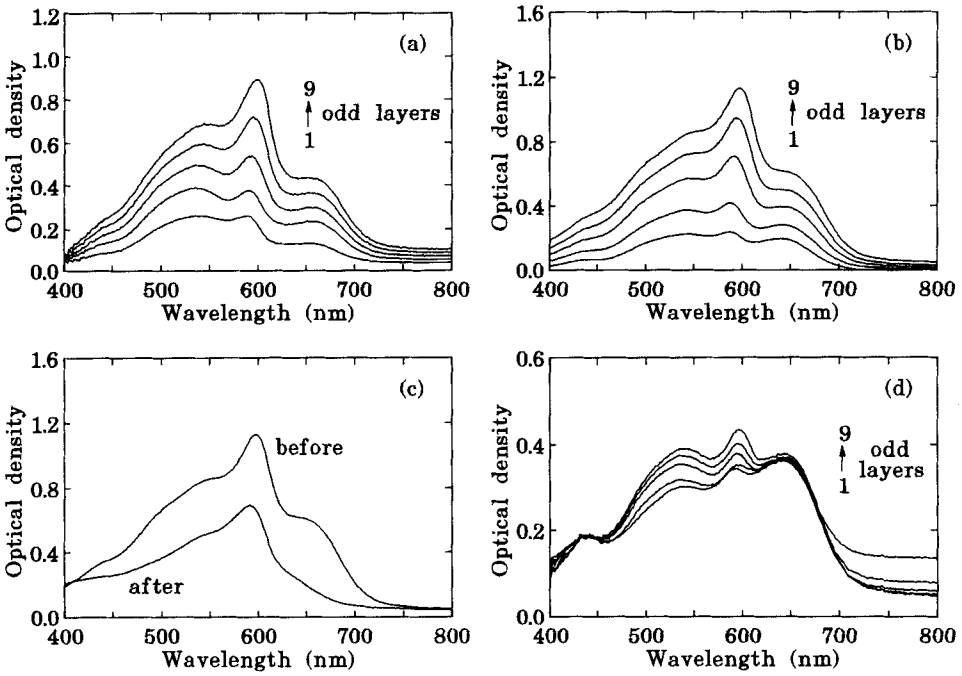

FIGURE 4 Absorption spectra of MG adsorbed $C_{18}MC$ LB films measured in the air.

(a) with no excitation light.

(b) with the 632.8nm excitation light during the deposition.

(c) before and after the 632.8nm irradiation for 90 minutes.

(d) with the 543.5nm excitation light during the deposition.

the irradiation of the excitation light for MG accelerates the decoloring of MG. Therefore, no influence of MG excitation during the deposition observed here might be due to the weakness of the irradiation power.

Figure 4(d) shows the absorption spectra of the adsorption LB films deposited with the 543.5nm light for $C_{18}MC$ excitation. The peaks of MG and $C_{18}MC$, in particular, J-band are observed weakly compared with that under no excitation light. It is considered that the irradiation of the excitation light for MC prevents the deposition of $C_{18}MC$. Furthermore, though the peak intensity of MC is increased with the number of LB layers, the peak intensity of MG is not changed. This phenomenon is not yet clear, but it is expecting method to control the molecular adsorption by the excitation light.

CONCLUSION

The authors have investigated the optical properties of $C_{18}MC$ LB films and MG adsorbed $C_{18}MC$ LB films deposited on the stripped core portions of the optical fibers. The absorption spectra of $C_{18}MC$ LB films show that the $C_{18}MC$ monolayer can be deposited onto the optical fibers and this measurement has high sensitivity. The MG adsorbed $C_{18}MC$ LB films show red-shifts due to the molecular interaction between $C_{18}MC$ and MG on the absorption spectra. Furthermore, the influence of the irradiation of the laser light for the molecular excitation during the deposition was discussed. These experimental results demonstrate that the in-situ optical monitoring using optical fibers is a powerful method to investigate the optical properties and the molecular interactions in the adsorption LB films.

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