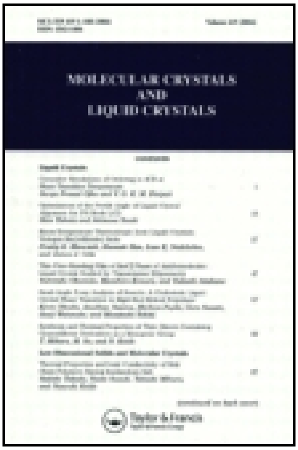

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Preparation and Optical Characterization of Hemicyanine Self-Assembled Monolayer on Au Substrate

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Abstract In order to construct hemicyanine self-assembled monolayers (SAMs), we have synthesized a hemicyanine with a disulfide group. Surface plasmon resonance spectroscopy and reflection absorption spectroscopy revealed formation of the hemicyanine monolayer array on the Au surface with simple immersion of the Au substrate in its ethanol solution. While many works have reported the association of H-aggregates in hemicyanine monolayers, we could not observe the H-aggregation in the present case.

Keywords hemicyanine; self-assembled monolayer; surface plasmon resonance

INTRODUCTION

Hemicyanine is so-called "push-pull" chromophore that possesses a large second-order molecular polarizability. A large amount of works has been carried out on hemicyanine Langmuir-Blodgett (LB) films and hemicyanine monolayers at the air-water interface.[1-4] However there is no report on the hemicyanine self-assembled monolayers (SAMs) on an Au surface. Since the nonlinear optical interaction between the chromophore and metal surfaces are interesting, it is important to establish such systems. Purpose of this work is to fabricate hemicyanine SAMs on an Au substrate to investigate optical response of a well ordered and densely packed two-dimensional nonlinear dipole array on metal surfaces. We synthesized the hemicyanine disulfide molecule and monitored the formation of the hemicyanine SAMs on an Au surface with use of *in-situ* surface plasmon resonance (SPR) spectroscopy and optical reflection absorption spectroscopy (RAS).

EXPERIMENTAL

The molecule used in the present study is depicted in Figure 1.

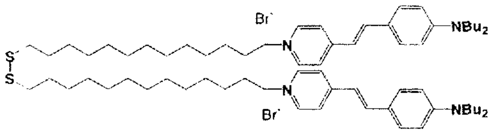

FIGURE 1 Chemical structure of the hemicyanine

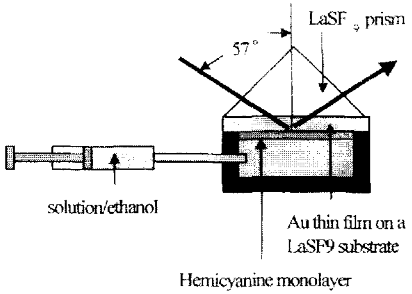

FIGURE 2 Optical setup for SPR study.disulfide molecule.

The synthesis will be reported elsewhere.[5] The substrate used in the present study was a 300 nm-thick Au thin film deposited on a glass substrate by vacuum evaporation. For the RAS measurement, the Au substrate was immersed in the ethanol solution of hemicyanine disulfide and was rinsed with ethanol carefully.

The SPR spectroscopy was accomplished with the optical geometry as shown in Figure 2. As a high index prism, LaSF9 glass was used. The Au-deposited LaSF9 glass plate was attached to the bottom of the prism with high index matching oil. A p-polarized semiconductor laser light (λ=670nm) was used to excite surface plasmon in the Au thin film, where the solution cell was located. Attenuated total reflection (ATR) scan was accomplished to evaluate an optical thickness of the sample. The reflectivity was monitored *in-situ* with time to investigate the adsorption process (Time scan measurement) at a certain angle of incidence. The RAS measurement was carried out with a MCPD-1000 multichannel spectrometer (Otsuka Electronics). The light was guided with a Y-type optical fiber normal to the substrate surface, and the reflected

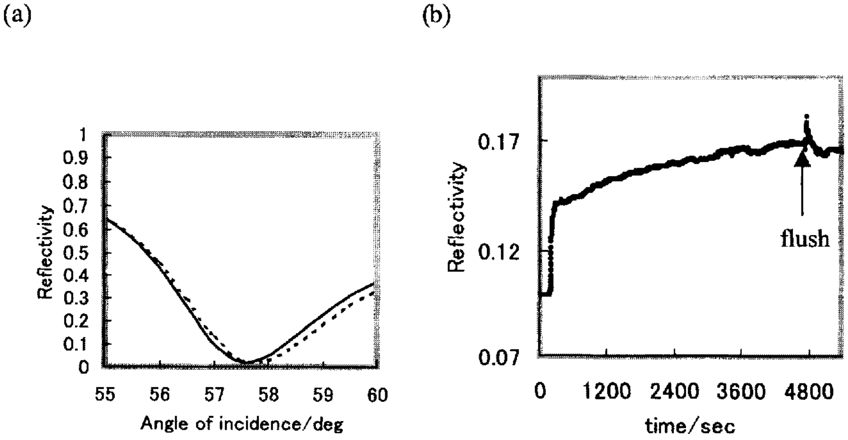

FIGURE 3 (a) The ATR scan profile of for the Au film (solid line) and the sample 5400 sec immersion in the solution (dashed line). (b) The result of the time scan measurement.

light was also detected with it.

RESULTS AND DISCUSSIONS

Figure 3(a) shows the results of the ATR scan for the bare gold surface and that for a the sample with the 90 min immersion in the 0.1 mM solution. The former ATR scan and the theoretical simulation deliver the optical constants (n_{Au}=0.18+4.05i) and the thickness of the Au film d_{Au}=42 nm used in this study. We used the index of the sample layer (n_{HEMI}=1.5) as a typical value for organic assemblies, because the absorption of the hemicyanine chromophroe is negligible at this wavelength λ=670 nm. With these values, the thickness of the sample was estimated to be 1.8 nm. This means that a densely packed monolayer was formed with 90 min-immersion of the Au substrate in the 0.1 mM solution, because the molecular model of the hemicyanine disulfide gives the length of the molecule l=2.1nm.

In order to investigate the adsorption process of the hemicyanine disulfide on an Au surface, we fixed the angle of incidence of 57 degree (at near resonance) and monitored the reflectivity with time. At t=194 sec, we injected the 0.1 mM hemicyinine solution. The reflectivity immediately increased with time until t=230 sec. Then the reflectivity was gradually increased and adsorption reached a platou at t=3000. Then we flushed the surface with ethanol.

Figure 4(a) shows the RAS spectrum for the sample with the 120 min immersion in the 0.1 mM solution. As previously reported,[6,7] the RAS spectrum is complicated due to the optical index of Au. To clarify the origin of this peak, we performed the simulation of the reflection absorption with the four layers model as described in Figure 4(b). We used the index of the Au thin film in literature.[8] The index of the hemicyanine SAM is evaluated with the Lorentz oscillation:

$$n_{\mathrm{SAM}} = n_{\mathrm{Lorentz}} + i n_{\mathrm{r}}$$

$$n_{\mathrm{Lorentz}} = \sqrt{\varepsilon + \frac{F}{\omega_0^{\,2} - \omega^2 + i\omega\Gamma}}$$

where Γ=5.58 x 10^{14} sec^{-1} ω_0=3.77 x 10^{15} sec^{-1} are evaluated from the absorption spectrum of solution, and F=5.0x10^{31} is from that of a hemicyanine monolayer LB film. As previously reported,[6,7] we used

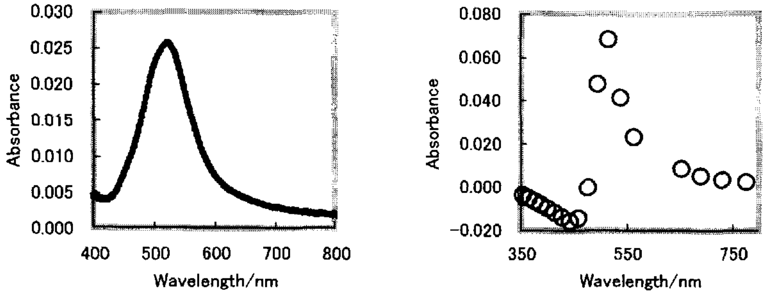

Figure 4 (a) The result of the RAS measurement for 120 min immersion in the 0.1mM solution. (b) The simulated result (see in the text).

n_r=0.8, which is mainly due to roughness factor of the Au surface. The results of the simulation represent the character of the reflection absorption spectrum, while some discrepancy arises from the simple model. The peak at 520 nm can be regarded as the surface plasmon resonance of the rough Au thin film, because this peak is also observed with the reflection absorption spectroscopy from oactadecanethiol SAMs on Au surfaces. The absorption cannot be observed as a peak at 500 nm because of the strong peak of surface plasmon at 520 nm. The simulation suggests that the resonance peak of hemicyanine at 500 nm is appeared as a dip at 420 nm, because the real part of the index of the SAM is minimum at this wavelength region.

In the previous study, pure hemicyanine monolyer LB films tend to form H-aggregates with a sharp absorption peak at 405 nm. However, in our result, no such absorption band and/or a sharp dip were in our reflection absorption spectroscopy. The difference in the chemical structure is the lenghth of the alkylchain attaching to the nitrogen atom of the amino group in the chromophoric part. It is likely that the *n*-butyl groups of the hemicyanine disulfide disturb the H-aggregation.

CONCLUSION

We report the successful fabrication of the hemicyanine SAM on Au substrate, which would be a good candidate to investigate nonlinear optical property of two-dimensional system on a metal surface. While the hamicyanine chromophore tend to associate H-aggregates in monolayers, we could not observe the H-aggregation in the present study probably due to the chemical structure. The study to control the H-aggregation is in progress, and will be reported elsewhere.

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