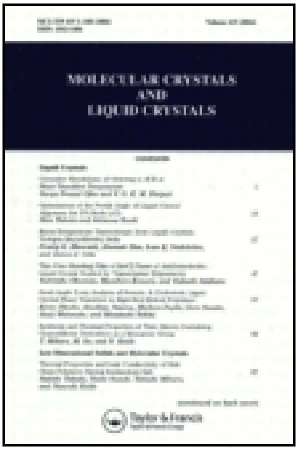

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TRANSIENT PHOTOCURRENT CHARACTERISTICS OF CHLOROPHYLL A LANGMUIR-BLODGETT FILM

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The transient photocurrent response of biodevice consisting of chlorophyll a Langmuir-Blodgett film was investigated. Chlorophyll a LB films were deposited onto the ITO coated glass. To confirm the film formation, surface analysis of chlorophyll a LB film was done by the measurement of scanning tunneling microscopy. Metal/insulator/metal structured biodevice was constructed by depositing aluminum onto the chlorophyll a LB film surface. To investigate the photoelectric response, action spectrum was measured at various wavelengths. The transient photocurrent characteristic was measured at various wavelengths by xenon lamp irradiation. Finally, the photoinduced charge transfer rates were measured using the transient photocurrent decay times. The proposed biodevice consisting of chlorophyll a could be applied to construct the molecular photonic device due to the photoinduced current flow.

Keywords: action spectrum; chlorophyll *a*; Langmuir-Blodgett; transient photocurrent

INTRODUCTION

The photochemical and photophysical behavior of biological pigments have been important subjects in the fields of photobiology and photochemistry [1–5]. Photoelectrichemistry is a well-established technique, which has been widely used to investigate the charge separation phenomena following the absorption of light on a modified electrode [6]. In connection with the photosynthetic primary process as well as light energy

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conversion, chlorophyll *a* (Chl *a*) has been one of the most widely studied pigments. From the absorption spectra of green plants, it has been revealed that multiple forms of chlorophyll (Chl) are present in green plants. It is also well known that Chl molecules on grana thylakoid membranes are arranged as a highly ordered state and the local concentration of porphyrin rings is relatively high [4]. Furthermore, reaction center Chl molecules, especially P700 in photosynthetic system I (PSI), would seem to have a specific structure due to the hydrophobic interaction between phytol chains and lipids/proteins, and an additional participation of hydrogen bonding.

In order to perform an *in vitro* investigation on the photoactivity of Chl *a*, several methods have been proposed to prepare the ordered structure of Chl *a*. There are two typical modes for fabricating a highly ordered structure of Chl *a* molecules; one is the incorporation of Chl *a* molecules into a small lipid bilayer, and the other is the deposition of ordered Chl *a* molecules onto solid substrates using Langmuir-Blodgett (LB) technique [7–10]. The *in vitro* photoelectrochemical behavior of the ordered structure of Chl *a* molecule has been observed, and its characteristics investigated for developing a model system for the primary photosynthetic process. The photoelectrical response such as the transient photovoltage at microsecond level and current-voltage characteristics at molecular level of the metal/insulator/metal (MIM) structured device consisted of Chl *a* LB film has been reported by the authors [11]. However, the photoelectrical response such as a transient photocurrent at various wavelengths and charge transfer rate of the metal/insulator/metal (MIM) structured device consisted of Chl *a* have not been reported yet.

In this study, the photoelectric responses of biodevice consisting of Chl *a* LB film are investigated for the application to molecular photonic device. To confirm the LB film formation, surface analysis is done by the observation of scanning tunneling microscopy (STM). Metal/insulator/metal structured device is fabricated by depositing aluminum onto the Chl *a* LB film surface. To investigate the photoelectric response, action spectrum is measured at various wavelengths. Finally, the transient photocurrent at various wavelengths was measured and the charge transfer rate of Chl *a* LB layer is calculated based on the decay time of transient photocurrent.

EXPERIMENTAL DETAILS

Chlorophyll *a* (Chl *a*, extracted from spinach) and chloroform were purchased from Sigma Chemical Co. (St. Louis, USA). For the deposition of Chl *a*, Au coated glass and ITO coated glass were used for the photoelectrical analysis. The LB film deposition of Chl *a* was carried out with a circular-type Langmuir trough (Model 2011, Nima Tech., UK). Chl *a* molecules were dissolved in chloroform at a concentration of 1 mM, and stored in a frozen state at -20°C without light illumination. Chl *a* solution was then carefully spread onto aqueous subphase (1 mM phosphate buffer pH7.0) at room temperature. Chl *a* molecules dispersed very rapidly and at the same time, the solvent evaporated from the subphase. After 20 min, monolayer of Chl *a* was compressed to dipping pressure at 25mN/m which were previously determined as the target pressure for optimal deposition [11]. The deposition of the Chl *a* LB films was started with an upward stroke. Thus the substrate was immersed into the subphase at first and the Chl *a* solution was applied onto the aqueous subphase. And then the layer was compressed to the target pressure and subsequently transferred to the substrate by moving the substrate upward using a computer-controlled stepping motor [7]. The dipping speeds of the upward and downward strokes for the Chl a LB film deposition were 4.5 and 5 mm/min, respectively. To fabricate the MIM structured biodevice, Al was vacuum deposited onto the Chl *a* LB film surface as the top electrode. The schematic structure of the biodevice consisting of Chl *a* LB film was shown in our previous report [11].

For the absorption spectrum measurement, the Chl *a* LB film was transferred onto quartz plate by using the previously described method, and their absorption spectrum was obtained using a UV/VIS spectrophotometer (V-550, JASCO, Japan) with a resolution of 1 nm. A bare-quartz was used as a reference. The experimental setup for the measurement of action spectrum and transient photocurrent response of the Chl *a* LB film was schematically illustrated in Figure 1. To measure the photoelectrical characteristics, 500 W xenon lamp (Model 66984, Oriel Co., USA) was used as a light source. The light from the xenon lamp was introduced to excite the Chl *a* LB film, and the photoexcited electrons of Chl *a* molecules were separated and transported to electrode. Action spectrum was measured by the storage oscilloscope of 500 MHz frequency (HP54616B, Hewlett-Packard, USA) connected to current preamplifier (SR240, Stanford Research, USA) at various wavelengths. To measure the transient photocurrent, light pulses were irradiated to Chl *a* LB layers by xenon lamp connected optical chopper (Scitec instruments, USA). Monochromatic light was illuminated onto the Chl *a* LB films using several optical filters, and the resulting photocurrents were analyzed. Pulse width and frequency were 0.2 ms and 20 Hz, respectively. With a fast preamplifier and a storage oscilloscope of 500 MHz frequency, the interlayer photocarrier movement was detected from a 50Ω strip line geometry in order to acquire signals with high time resolution. All electrical measurements were carried out in open air at room temperature.

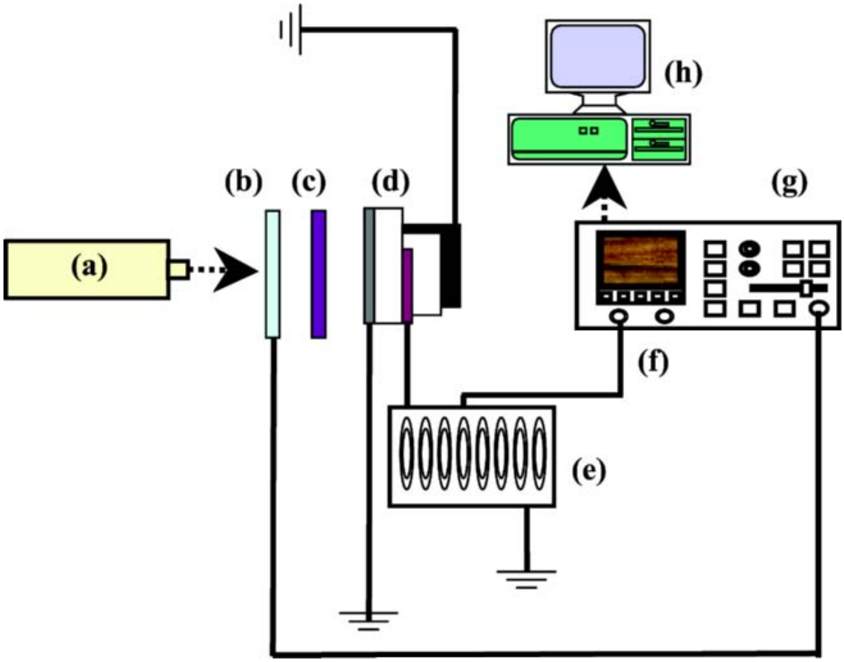

FIGURE 1 The schematic illustration for the transient photocurrent measurement; (a) 500 W xenon lamp, (b) optical chopper, (c) optical filter, (d) sample device, (e) current preamplifier, (f) signal input, (g) oscilloscope, (h) data acquisition.

RESULTS AND DISCUSSION

To verify the Chl *a* LB film formation, surface morphology was observed by scanning tuneling microscopy (STM, AutoProbe CP, PSI, USA) using constant current mode. In Figure 2, Chl *a* LB film has $10 \sim 30$ nm scale molecular cluster. Considering the size of Chl *a* molecules, it is indicated that the Chl *a* molecules form the aggregates at langmuir monolayer formation on the subphase.

In order to confirm the deposition of Chl *a* LB layers onto a solid substrate, the absorption spectrum of the Chl *a* LB film was measured. As shown in Figure 3(a), the absorption spectrum of the Chl *a* LB film was fairly consistent with that of the Chl *a* solution. It has a broad band ranging from 400–700 nm with two specific peaks at around 438 nm and 666 nm, respectively. Also, the tendency of the absorption spectrum of Chl *a* LB film is similar to the solution, it is indicated that the Chl *a* molecules form the layer and preserve the absorption property on solid substrate. In order to

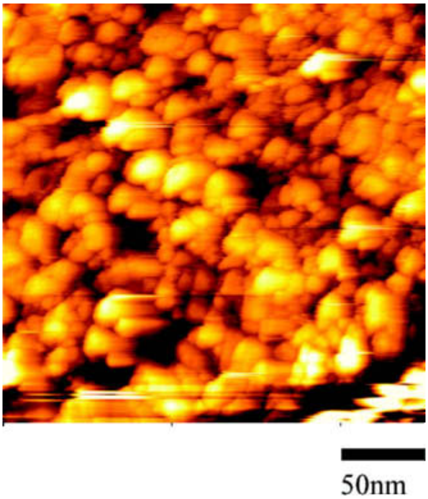

FIGURE 2 500 nm Scan size surface morphology of Chl *a* LB layer by AFM.

confirm whether the photocurrent generation of Chl *a* LB film reflects the light-energy conversion mechanism, the action spectrum of the Chl *a* LB film should be obtained. Using a series of monochromatic light illuminations, the action spectrum was obtained and shown in Figure 3(b). As the saturation of photocurrent signal was reached in similar times, the current intensities at various wavelengths could be used to obtain the action spectrum. Also, the action spectrum intensities of Chl *a* LB film are similar to the maximum absorption peaks. It is indicated that the absorbance influences the photocurrent intensity.

To prove the existence of an internal electric field and its influence on creation of the photoinduced charge transfer in the Chl *a* LB films, the transient photocurrent at various wavelengths was measured and analyzed as shown in Figure 4. By light illumination, the electrons of Chl *a* molecules were excited from their ground state to excite state (Chl a^*). The photoexcited electrons returned to their ground state and then red shifted fluorescence emitted. However the metal electrode or electron acceptor was exposed to excited Chl *a*, some of photoexcited electrons of Chl a^* were separated and transferred to electrode or electron acceptor. Thus the photoinduced electron flow could be generated. By measuring the transient photocurrent, the electron transfer rate of Chl *a* molecule could be calculated and the photoinduced electron transfer could be verified. The photocurrent signals were formed quickly and then decayed in the time constant. The shapes and intensities of decay profiles were similar to

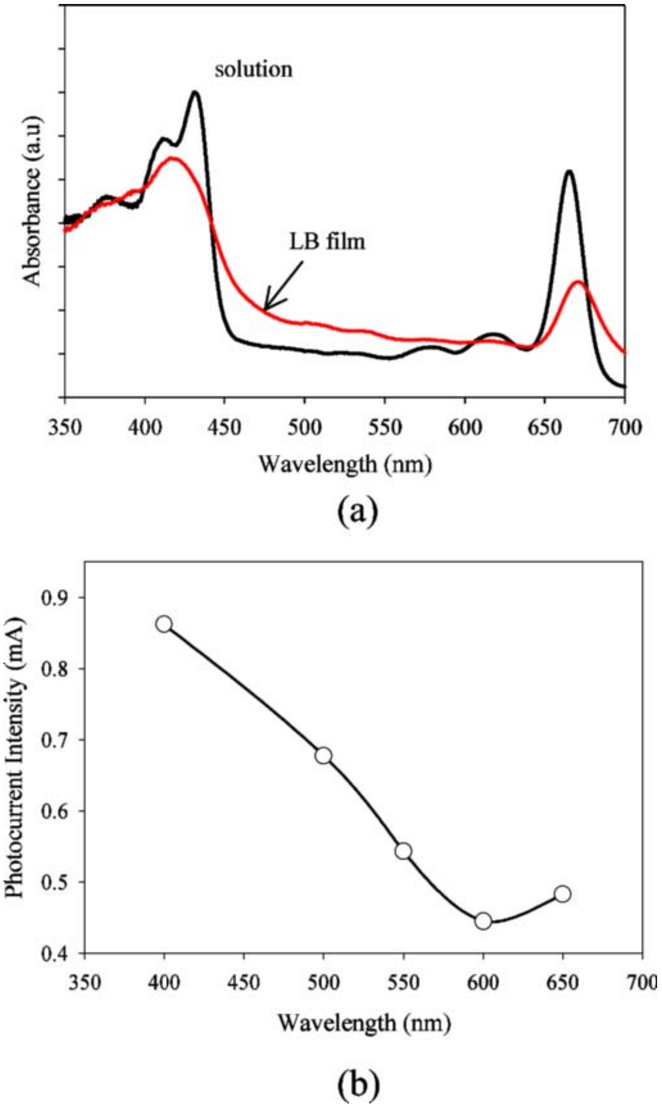

FIGURE 3 (a) Absorption spectrum of Chl *a* solution and LB film (20layer), (b) action spectrum of Chl *a* LB film.

the action spectrum of Chl *a* LB film. Though the initial rise of the transient photocurrent has concerned with the charge separation rate, the charge separation rate cannot be calculated by transient photocurrent measurement due to the sub-nanosecond order of time constant. The charge transfer rate could be calculated with the decay profile of transient photocurrent

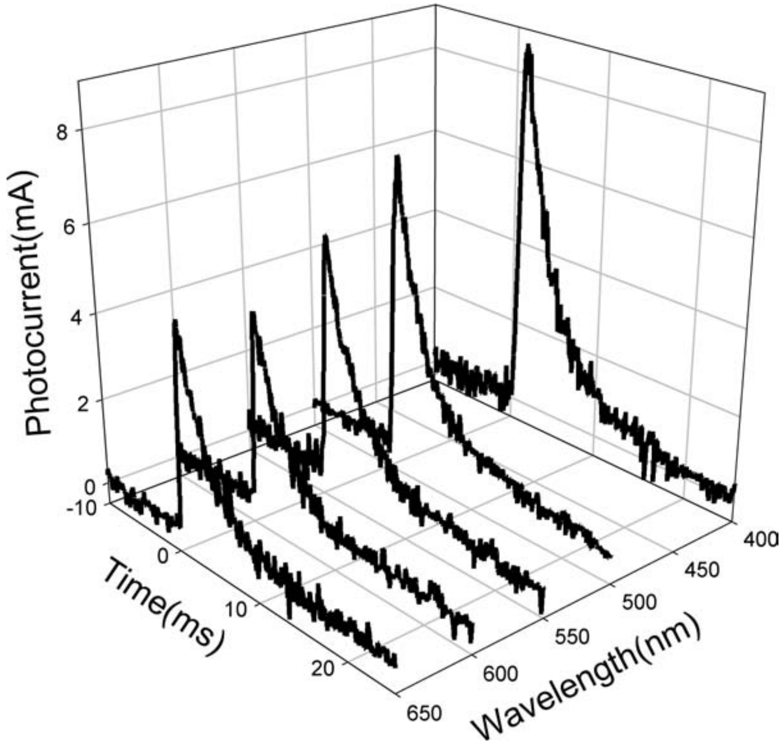

FIGURE 4 Transient photocurrent decay profiles of Chl *a* LB film.

due to the ms order of time constant. The decays of transient photocurrents of Chl *a* LB films were fitted with single exponential function, in which the exponent was the decay time constant. From the time constants, the charge transfer rates in the Chl *a* LB film could be calculated since the inversion of time constant was the charge transfer rate [12–15]. The decay time constants and charge transfer rates of photocurrents were shown in Table 1. Photocurrent signals of Chl *a* LB film have single decay components. It is indicated that the photoexcitation for Chl *a* LB layer

TABLE 1 Decay Time Constant of Photocurrent and Charge Transfer Rates of Chl *a* LB Film

Wavelength	400	500	550	600	650
Decay time constant (ms)	3.446	3.203	4.289	3.818	4.102
Charge transfer rate $\times 10^4$ (s^{-1})	2.9	3.12	2.33	2.62	2.44

should generates the one-way charge (current) flow. The shape and intensity of this component was dependent on the action spectrum of Chl *a* LB film. These results seem to suggest that the photoinduced excitation of Chl *a* LB film is the initial process of the charge carrier mechanism, which generates the current flow across the Chl *a* LB film. Consequently, it would appear that the photocurrent generation of Chl *a* LB films mainly rely on the photoelectric conversion.

CONCLUSIONS

Molecular films of chlorophyll *a* (Chl *a*) were prepared by Langmuir-Blodgett (LB) film technique. The MIM structured biodevice consisting of Chl *a* LB film was fabricated for the photoelectric property measurement. The charge transfer rate of Chl *a* LB layer was calculated and the photoinduced electron transfer could be verified based on the transient photocurrent profile. It can be concluded that the molecular layer of Chl *a* could be applied to construct the biomolecular photonic device due to photoinduced current flow at various wavelengths.

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