J. Microbiol. Biotechnol. (2004), **14**(5), 1038–1042

JOURNAL OF MICROBIOLOGY AND BIOTECHNOLOGY

Photoswitching Characteristics of Biodevice Consisting of Chlorophyll *a* Langmuir-Blodgett Film

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Received: June 23, 2003
Accepted: November 28, 2003

Abstract The photoelectric responses of a biodevice consisting of chlorophyll *a* Langmuir-Blodgett film were investigated. Chlorophyll *a* Langmuir-Blodgett films were deposited onto ITO and Au coated glass. To confirm film formation, surface analysis of chlorophyll *a* Langmuir-Blodgett film was carried out by measurement using atomic force microscopy. The metal/insulator/metal structured biodevice was constructed by depositing aluminum onto the chlorophyll *a* Langmuir-Blodgett film surface. To investigate the photoelectric response, the current-voltage characteristic was measured by the conducting metal tip. The photoswitching function and transient photovoltage characteristics of the proposed device were measured by irradiation with Ar ion laser and N_2 pulse laser, respectively. This research suggested that the proposed biodevice consisting of chlorophyll *a* could be applied to the molecular scale biosensor and/or bioelectronic device.

Key words: Chlorophyll *a*, Langmuir-Blodgett, photoswitching, transient photovoltage

The photochemical and photophysical behavior of biological pigments have been important subjects in the fields of photobiology and photochemistry [1, 5, 6, 9, 10]. In connection with the photosynthetic process as well as light energy conversion, chlorophyll *a* (Chl *a*) has been one of the most widely studied pigments. From the absorption spectra it has been revealed that multiple forms of chlorophyll (Chl) are present in green plants. It is also well known that Chl molecules on thylakoid membranes are arranged in a highly ordered state and that the local concentration of porphyrin rings is relatively high [9]. Furthermore, reaction center Chl molecules, especially P700 in photosynthetic system I (PSI), have a specific structure due to the hydrophobic interaction between phytol chains and lipids/proteins as well as the participation of hydrogen bonding.

In order to perform an *in vitro* investigation on the photoactivity of Chl *a*, several methods have been proposed for the preparation of 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 the Langmuir-Blodgett (LB) technique [2, 7, 8, 12]. We have investigated many types of biodevices such as a biosensor, a biochip, and a bioelectronic device [3, 4, 11]. The *in vitro* photoelectrochemical behavior of the ordered structure of Chl *a* molecule has been observed, and its characteristics were investigated for developing a model system for the primary photosynthetic process [2]. However, photoelectrical responses such as the transient photocurrent at the microsecond level and current-voltage characteristics at the molecular level of the metal/insulator/metal (MIM) structured device consisted of Chl *a* LB film have not been reported.

In this study, the photoelectric response characteristics of biodevices consisting of Chl *a* LB film were investigated for their application to artificial molecular photonic devices. The current-voltage characteristics of Chl *a* LB film at the molecular level were investigated using the conducting atomic force microscopy (AFM) probe as a top electrode. The photoswitching function and transient photovoltage were investigated by the irradiation of 488 nm Argon (Ar) ion laser and 335 nm N_2 pulse laser, respectively. Chlorophyll *a* (Chl *a*, extracted from spinach) and chloroform were purchased from Sigma Chemical Co. (St. Louis, U.S.A.). For the deposition of Chl *a*, Au coated glass and indium tin oxide (ITO) coated glass were used for photoelectrical analysis. The LB film deposition of Chl *a* was carried out with a circular-type Langmuir trough (Model 2011, Nima Tech., U.K.). Chl *a* molecules were dissolved in chloroform at a concentration of 1 mM, and stored in a frozen state at

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-20°C without light illumination. Chl *a* solution was then carefully applied onto an aqueous subphase (1 mM phosphate buffer pH 7.0) at room temperature, and the resulting monolayers were compressed to dipping pressure at 25 mN/m [2]. The deposition of the Chl *a* LB films was started with an upward stroke. Thus, the substrate was first immersed into the subphase and the Chl *a* solution 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 [2]. 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, aluminum (Al) was vacuum deposited onto the Chl *a* LB film surface as a top electrode. The schematic structure of the biodevice consisting of Chl *a* LB film is shown in Fig. 1. The experimental setup for the measurement of the current-voltage response of the prepared Chl *a* LB film is schematically illustrated in Fig. 2. The conducting AFM probe was used to verify the current-voltage characteristics at molecular scale. A current-voltage (I-V) measuring unit (SMU Model 236, Keithley, U.S.A.) was used as a bias source for current measurement. A conducting AFM tip (Ultra Lever Non-Contact Mode Magnetic Force Microscopy, ThermoMicroscopes, U.S.A.) was used as a top electrode for the current-voltage measurement of the Chl *a* LB film. and Au substrate was used as a bottom electrode. Electrical resistance between the AFM tip and the Au substrate was more than 10 MΩ in 0 V. The current and approaching force were measured when the conducting AFM tip was moved toward the sample surface. The set point for the AFM tip approached was 20 nN and the scan range for the

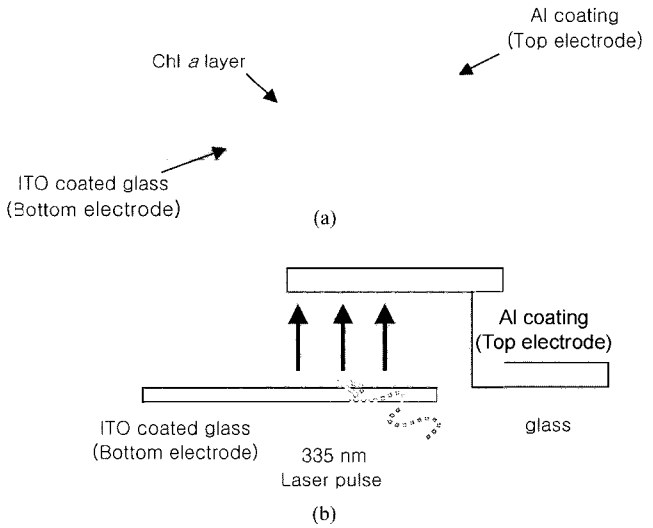

Fig. 1. The schematic structure of the biodevice consisting of Chl *a* LB film. (a) Top view; (b) Side view.

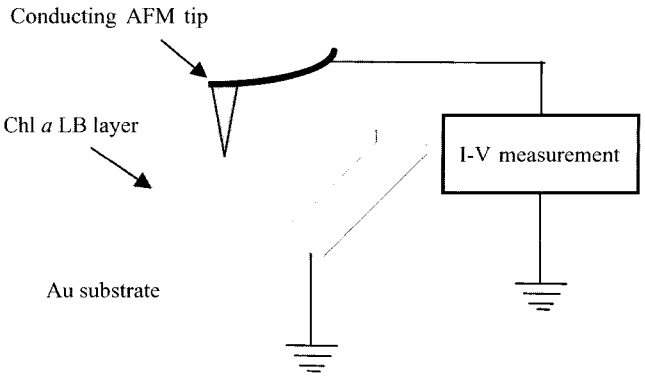

Fig. 2. Experimental setup for the measurement of the current-voltage response of the prepared Chl *a* LB film.

current-voltage measurement was -1~1 V. In Fig. 3, the experimental setups for the photoswitching and transient photovoltage measurement are illustrated. To measure the photoswitching function, an Ar ion laser system at 488 nm high power was used. The laser light from the Ar ion laser system was introduced to excite the Chl *a* LB film. The photoswitching function was measured with

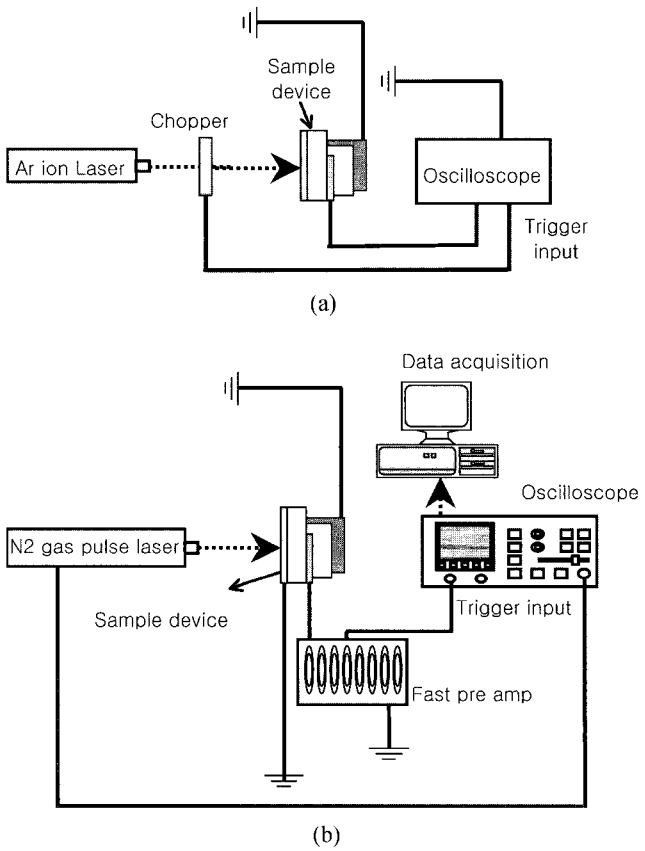

Fig. 3. Experimental setup for the (a) photoswitching function and (b) transient photovoltage measurement.

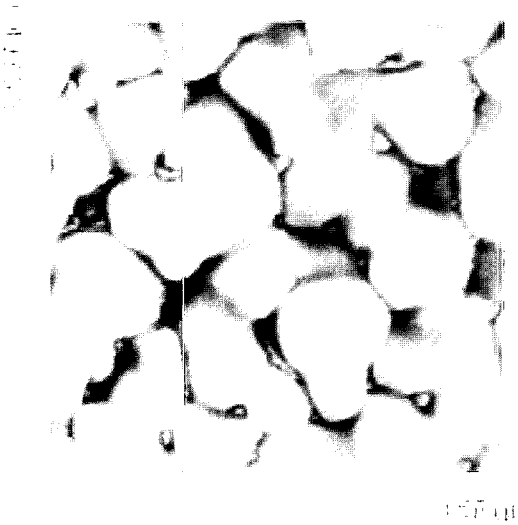

Fig. 4. 500 nm scan size surface morphology of the Chl *a* LB film by AFM.

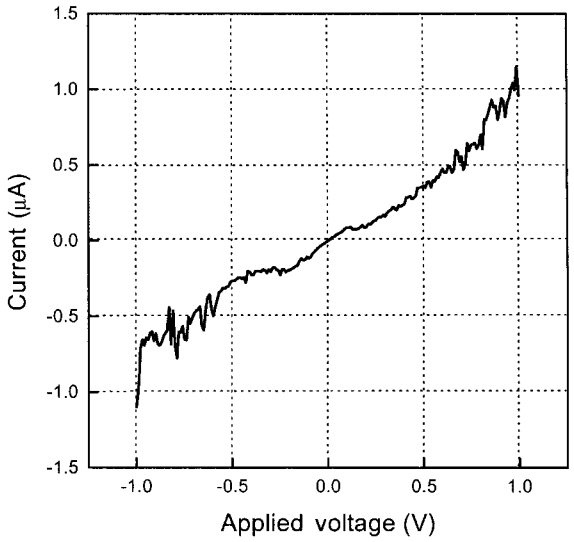

Fig. 5. Current-voltage characteristic of the Chl *a* LB monolayer.

a storage oscilloscope of 500 MHz frequency (HP54616B, Hewlett-Packard, U.S.A.). To measure the transient photovoltage at 335 nm, a low power N_2 gas pulse laser system was used. The light pulse from the laser system consisting of a N_2 gas laser (6 mW, 400 mj, VSL-337ND, LSI, U.S.A.) was introduced to excite the Chl *a* molecules. The pulse width and frequency were 10 ns and 200 Hz, respectively. With a fast preamplifier (Model SR 240, Stanford Research, U.S.A.) and a storage oscilloscope of 500 MHz frequency, the interlayer photocarrier movement was detected from a 50 Ω strip line geometry in order to acquire signals with high time resolution.

To verify the LB film formation, the surface morphology of the Chl *a* LB film was obtained by AFM. In Fig. 4, Chl *a* LB film has a 100 nm scale molecular cluster. It is indicated that the Chl *a* molecules were aggregated before Langmuir monolayer formation on the aqueous subphase.

By approaching the conducting AFM tip onto the Chl *a* LB monolayer surface, the current-voltage characteristic at the molecular level was obtained in ambient condition as shown in Fig. 5. When a forward bias was applied in a range of 0~+1 V, current was generated with the appropriate bias voltage. Less current was generated in the backward environment in the range of 0~- 1 V. When +1 V of forward bias was applied to the Chl *a* LB film with a 20 nN set point, the current was generated with 1.1 μA. Otherwise, when - 1 V of reverse bias was applied, the current was - 1.0 μA. The current intensity generated in the forward and backward bias of the Chl *a* LB film was almost the same within the acceptable error range. The results suggested that the molecular layer of Chl *a* could be applied to construct the biomolecular electronic device due to current flow at a molecular level. The photoswitching response of the proposed biodevice consisting of Chl *a* LB film is shown in Fig. 6. When a forward bias was applied, a photovoltage was generated. With repeated step illumination, a reproducible photovoltage was generated. This result indicates that the photoswitching function of the biodevice was achieved. It was also observed that the photovoltage intensity was dependent on the LB film thickness. The thicker the LB film layer used, the higher the photovoltage was generated. In order to investigate the charge transfer in the Chl *a* LB films, the transient photovoltage was measured and analyzed as shown in Fig. 7. By light illumination, the electrons of Chl *a* molecules were excited from their

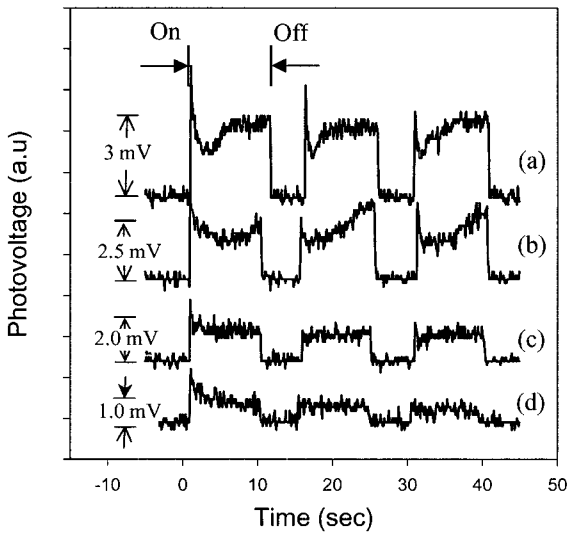

Fig. 6. Photoswitching response of the proposed biodevice consisting of Chl *a* LB film. a, 4-layer; b, 3-layer; c, bilayer; d, monolayer.

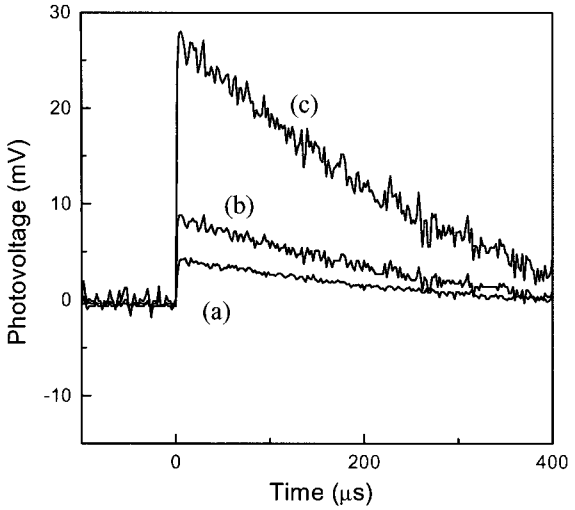

Fig. 7. Transient photovoltage of Chl *a* LB film. a, Monolayer; b, bilayer; c, 5-layer.

ground state to an excited state (Chl *a**). The photo-excited electrons returned to their ground state and red shifted fluorescence was then emitted. However, when the metal electrode or electron acceptor was exposed to excited Chl *a*, some of the photo-excited electrons of Chl *a** were separated and transferred to an electrode or electron acceptor. In this way photo-induced electron flow could be generated. By measuring the transient photovoltage, the electron transfer rate of the Chl *a* molecules could be calculated and the photoinduced electron transfer could be verified. Figure 7 shows the transient photovoltage of the Chl *a* LB film. The photovoltage signals were formed quickly and then decayed with a time constant. Though the initial rise of the transient photovoltage is related to the charge separation rate, it cannot be calculated due to the sub-nanosecond order of time constant. On the other hand, the charge transfer rate could be calculated with the decay profile of transient photovoltage due to the μs order of time constant. The decays of transient photovoltages of Chl *a* LB films were fitted with a double exponential function, in which the exponent was the decay time constant. The Chl *a* LB monolayer has a flat structure and exhibits low signal intensity, while in the bilayer, the interlayer interaction improves the signal intensities two-fold. With a further increase in the number of layers, the signal intensities still increase, and yielding signals are increased five-fold for films with 5 layers as compared with those of monolayer structure. The transient photovoltage signals of Chl *a* LB films consisted of two components. The fast component was observed in a time domain of 1-100 μs and the slow decay component was observed in a time domain of >>100 μs. The shape and intensity of this component was dependent on the thickness of Chl *a* LB film. The decay time constant of the fast component of photovoltage was about 46.3, 57.9, and 77.1 μs for the monolayer, bilayer, and 5 layers of Chl *a* LB film, respectively. Using the time constant, the charge transfer rate in the Chl *a* LB film could be calculated since the inversion of time constant was the charge transfer rate. The charge transfer rate in the Chl *a* LB film was about 21.58×10^{-3}, 17.27×10^{-3}, and 12.96×10^{-3} μs^{-1} for the monolayer, bilayer, and 5 layers of Chl *a* LB film, respectively.

Molecular films of chlorophyll *a* were prepared by the Langmuir-Blodgett film technique. The MIM structured biodevice consisting of Chl *a* LB film was fabricated for photoelectric property measurement. The current-voltage characteristic of Chl *a* LB film deposited onto Au substrate was investigated using the conducting AFM tip as the top electrode. Photocurrent generation at a molecular level was observed with forward and backward bias to the Chl *a* LB film. The photoswitching function of the proposed biodevice consisting of an Al top electrode/Chl *a* LB film/ ITO coated glass was achieved. The charge transfer rate of the Chl *a* molecule was calculated and the photoinduced electron transfer could be verified based on the transient photovoltage profile. It can be concluded that the molecular layer of Chl *a* could be applied to a biosensor and/or biomolecular electronic device due to current flow at a molecular level.

Acknowledgments

This work was supported by grants from the contribution of Advanced Backbone IT Technology Development Project (IMT2000-B3-2) of the Ministry of Information & Communication and supported by the Sogang University Research Grants in 2003.

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