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Photoelectrochemical Behavior of Chlorophyll *a* Langmuir-Blodgett Films

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Abstract

The highly efficient photoelectric conversion of chlorophyll *a* (Chl *a*) monolayers and multilayers was investigated. Using the Langmuir-Blodgett (LB) technique, Chl *a* monolayers and multilayers were fabricated onto optically transparent electrode, such as ITO glass. The photocurrent could be observed according to the light illumination. The action spectrum of the Chl *a* LB films was well consistent with its absorption spectrum. The possible application of the proposed system as a constituent of the artificial color recognition device was suggested.

Introduction

Photochemical and photoelectric behavior of biological pigments have been the subjects in the fields of photobiology and photochemistry[1,2]. In the connection with the photosynthetic primary process as well as light energy conversion, chlorophyll *a* (Chl *a*) has been one of the most widely studied pigments. *In vitro* photoelectrochemical behaviour of Chl *a* has been studied since the early 1970's. It is known that Chl *a* molecules on grana thylakoid membranes assume a highly ordered state and the local concentration of porphyrin rings is relatively high. Furthermore, reaction center Chl *a* molecules are supposed to have a specific structure due to hydrophobic interaction between phytol chains and lipids/proteins, and an additional participation of hydrogen bonding.

In vitro investigation on the photoactivity of the ordered structure of Chl *a* has been performed with two modes, the incorporation of Chl *a* molecules into a small lipid bilayer and the deposition of ordered Chl *a* molecules onto solid substrates by Langmuir-Blodgett (LB) technique. The photoelectric conversion of the ordered structure of Chl *a* molecules was observed, and its characteristics were used as a model system of the primary photosynthetic process. However,

further applications to other field, such as bioelectronics, have rarely been reported.

In the present work, the photoelectrochemical behaviour of Chl *a* monolayers and multilayers was investigated. Based on the resulting photocurrent, the possible application of Chl *a* LB films as a constituent of the artificial color recognition device was also suggested.

Materials and Methods

Chlorophyll *a* (Chl *a*) extracted from spinach, benzene, and other miscellaneous reagents were purchased from Sigma Chemical Co. (St. Louis, USA). With a circular-type Langmuir trough (Model 2011, Nima Tech., UK), Chl *a* LB films were prepared onto optically transparent ITO glass. The fabricated Chl *a* monolayers and multilayers were set into an electrochemistry cell equipped with Pt plate as a counter electrode. KCl solution (0.1 M) was used as a supporting electrolyte. According to the light illumination with a 300 W Xenon lamp (Oriel Co., USA), the photocurrent generation was observed and analyzed with a current preamplifier (SR570, Stanford Research System, USA), an oscilloscope (HP54610B, Hewlett Packard, USA), and a personal computer.

Results and Discussion

The absorption spectra of Chl *a* in solution state and solid-like state (LB films) were shown in Figure 1. The absorption spectrum of Chl *a* LB films was well consistent with that of Chl *a* in solution state. The absorption peaks were found at 678 and 438 nm, respectively. It was observed that there were the slight red-shifts by 10 ~ 15 nm, which are well consistent with the previously reported ones[1,2]. This results might be due to the close-packed structure of the Chl *a* LB films.

Figure 2 shows the typical photoelectric response of Chl *a* LB films and its light intensity dependency. The typical response of Chl *a* LB films was anodic, and the magnitude of photocurrent was found as about 22 nA/cm^2 when 5 layers were deposited. Compared with other light-sensitive pigments, the electron injection from the excited state of Chl *a* shows relatively high efficiency. The photocurrent generation was gradually increased with the incident light intensity as shown in Figure 2(b). Based on this linear relationship, it is suggested that the Chl *a* LB films can be used as a component of artificial

photoreceptor.

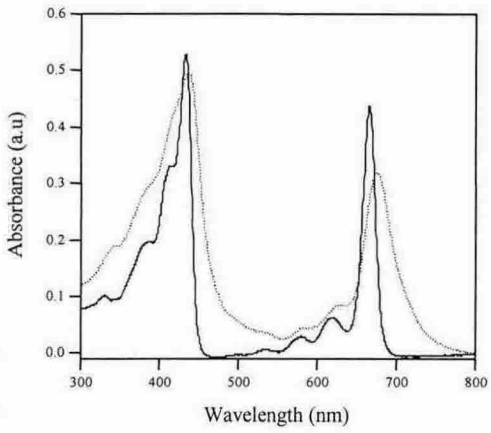

Figure 1. Absorption spectra of Chl *a*; solid line, absorption spectrum of Chl *a* solution; dotted line, absorption spectrum of Chl *a* LB films (10 layers).

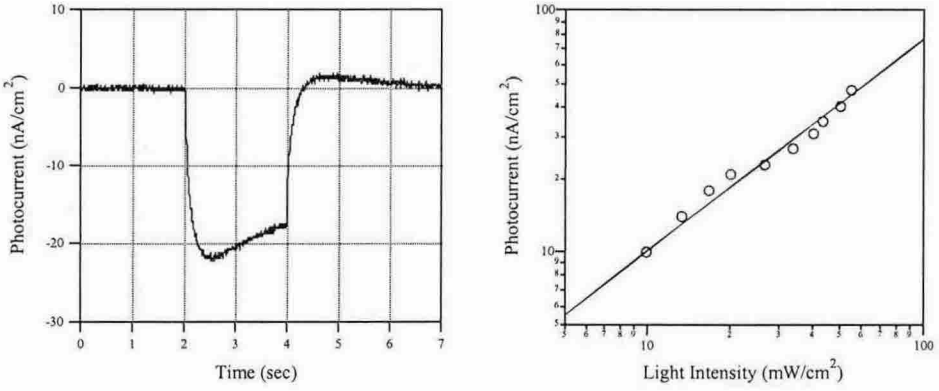

Figure 2. (a) Typical photoelectric response of Chl *a* LB films (5 layers); (b) Photocurrent generation of Chl *a* LB films (10 layers) as a function of light intensity.

Figure 3 shows the action spectrum of Chl *a* LB films. The action spectrum of Chl *a* LB films was well coincide with the absorption spectrum, showing the maxima at around 430 and 680 nm. It could be observed that the action spectrum of Chl *a* LB films has relatively broad range in the visible region. It is suggested that the color recognition would be possible if the photoelectric response characteristics of Chl *a* LB films is combined with other light-sensitive

pigment that responds according to the green light illumination, i. e. bacteriorhodopsin (bR). For a further application of Chl *a* LB films as a color recognition bioelectronic device, the combined response characteristics of two molecules should be elucidated.

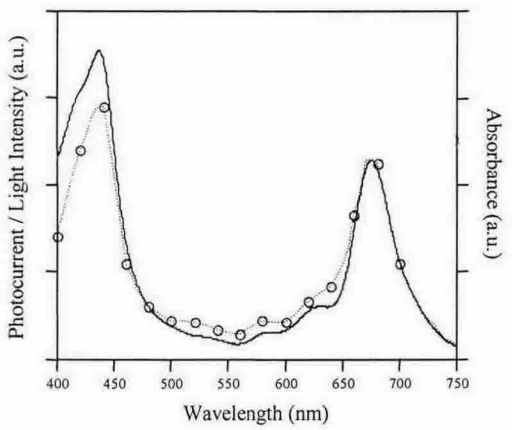

Figure 3. Action spectrum of Chl *a* LB films; solid line, absorption spectrum; dotted line, action spectrum.

Acknowledgment

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References

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