

PHOTOELECTROCHEMICAL STUDY ON CHLOROPHYLL MONOLAYER ELECTRODES

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Anodic photocurrents and negative photovoltages were observed upon irradiation to chlorophyll (Chl) a and b monolayers deposited on SnO₂ optically transparent electrodes in an electrochemical cell. Photocurrent quantum efficiency was measured with Chl a-stearic acid mixed monolayers and a highest value of 12-16 % was attained.

Photochemical and photoelectric behaviors of in vitro Chl have been the subject of a number of recent works related to the primary light reaction of photosynthesis. In many cases, photocurrents have been measured with an aggregated Chl formed on a metal electrode by solvent evaporation,¹⁾ or with an electrodeposited microcrystalline Chl.²⁾ Similar investigations were carried out by other workers.³⁾⁻⁵⁾ However, as is well known, Chl molecules in chloroplasts of green plants are in two-dimensionally ordered state. Therefore it would be preferable to use as the photoreceptor an ordered Chl layer, instead of aggregates, for an in vitro simulation of primary processes in photosynthesis. One mode for the preparation of such an ordered Chl layer is the incorporation of Chl molecules into a bilayer lipid membrane, as have been reported by Chen and Berns.⁶⁾ In this case, however, the observed photoconversion efficiency was quite low presumably due to the inherent high resistivity of the lipid layer.

As another mode, one can construct a Chl monolayer on a solid substrate by means of the Langmuir-Blodgett technique.^{7),8)} A metal appears to be inappropriate as the substrate in this case, since the excited state of Chl would be quenched very efficiently by free electrons in the metal.⁹⁾ These considerations have led us to use an SnO₂ optically transparent electrode (OTE) as the substrate for monolayer deposition. Electron injection from excited dyes to the conduction band of an SnO₂ electrode takes place with high efficiency,¹⁰⁾ and a backward electron flow can be suppressed because of the rectifying property of the semiconductor-solution interface.

Chl a and b were prepared from spinach with the dioxane method¹¹⁾ followed by a column chromatography on sucrose. The SnO₂ OTE employed was 2000 Å thick, on a glass support, and had a donor density of ca. 10^{20} cm⁻³ and a specific resistance of 4×10^{-3} ohm-cm. Monolayers of Chl a and b were formed by spreading 10^{-4} M benzene solution on the aqueous phase (10^{-3} M phosphate buffer, pH 7.2) in a Langmuir trough equipped with a film balance (Kyowa Kagaku, Ltd), and were deposited onto the SnO₂ OTE under a constant surface pressure.⁷⁾ In order to control the surface concentration of Chl a, mixed monolayers of Chl a-stearic acid (C₁₈) were formed and deposited in a similar manner. Absorbance of monolayers at SnO₂/air and SnO₂/electrolyte interfaces

were measured by alignment of several electrodes in parallel on a Shimadzu spectrophotometer Model MPS-5000. The SnO_2 OTE (working electrode) was mounted as a window of an electrochemical cell, with the Chl-deposited side facing the electrolyte solution. A platinum wire and an SCE served as the counter electrode and the reference electrode, respectively. The solution, being always flushed with high purity nitrogen, contained 0.05-0.1 M Na_2SO_4 as a supporting electrolyte and 0.05-0.1 M hydroquinone (H_2Q) as a reducing agent. In most cases the pH of the electrolyte was controlled with a phosphate buffer. As the light source, a 500 W xenon arc lamp was used in combination with a Shimadzu grating monochromator. Photocurrents were measured with a Keithley picoammeter Model 417 under potential-controlled condition (by means of a Hokuto Denko potentiostat Model HA-101), and open-circuit photovoltages were detected with a Keithley electrometer Model 610B.

First, the surface pressure-area isotherm of a Chl a monolayer on an aqueous phase was examined. The monolayer remained stable at pressures below 24 dyn/cm. At 20 dyn/cm, where most of our Chl a monolayer depositions were performed, the area occupied by a Chl a molecule amounted to ca. 100 \AA^2 . At the SnO_2 /air interface, the absorption peaks were found at 676 and 437 nm with respective absorbance of 0.0082 and 0.0103 per layer. These characteristics are in fair agreement with the reported ones.⁸⁾ Immersion of the Chl a-deposited SnO_2 electrode in an electrolyte solution resulted in a general decrease in the absorbance by 20-40 % accompanied by a slight hypsochromic shift of the absorption peaks, which could be mostly restored by subsequent drying. The reason for such spectral changes remains unclarified at the present stage.

Upon irradiation to the Chl-deposited SnO_2 OTE, anodic photocurrents were always observed under potentiostatic as well as short-circuit conditions. The photocurrent

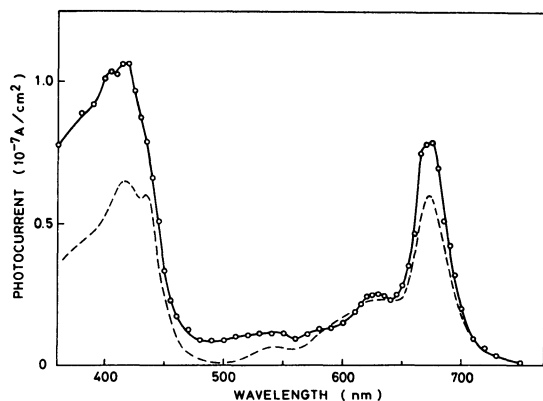


Fig. 1. Photocurrent spectrum at Chl a monolayer. Surface pressure for deposition, 20 dyn/cm; electrolyte, H_2Q 0.05 M, Na_2SO_4 0.05 M and phosphate buffer 0.025 M (pH 6.9); electrode potential, +0.05 V vs. SCE. The dashed curve represents the absorption spectrum of a Chl a monolayer at SnO_2 -electrolyte interface.

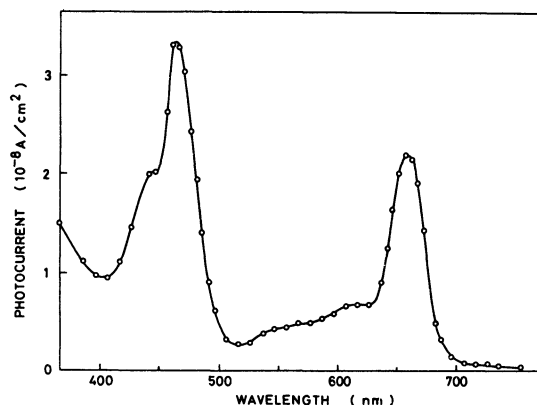


Fig. 2. Photocurrent spectrum at Chl b monolayer. Surface pressure for deposition, 10 dyn/cm; electrolyte, H_2Q 0.1 M and phosphate buffer 0.025 M; electrode potential, +0.05 V vs. SCE.

showed no decay for more than 7 hours if the electrolyte solution contained H_2Q to a sufficient concentration. The magnitude of the photocurrent was proportional to the incident light intensity. Figure 1 shows a typical photocurrent spectrum, corrected for the photon flux to $1.4 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$. As seen in the figure, the photocurrent spectrum fairly coincides with the absorption spectrum of Chl a at the SnO_2 /electrolyte interface, showing maxima at 415-420 and 672-675 nm. Figure 2 depicts a similar photocurrent spectrum observed with a Chl b monolayer deposited on an SnO_2 electrode. In this case the maxima are situated at 463 and 657 nm. Open-circuit photovoltages were always negative, in accordance with the anodic photocurrent (electron injection to SnO_2). The photovoltage spectrum for Chl a also agreed fairly well with the absorption spectrum.

Dependence of the photocurrent due to Chl a excitation on the electrode potential is illustrated in Fig. 3. The photocurrent rises at -0.17 V vs. SCE, slightly more anodic than the flatband potential of the SnO_2 electrode, and increases with the anodic polarization until a maximum is reached at ca. +0.1 V vs. SCE. The subsequent decrease of the photocurrent above +0.1 V may be due to the oxidation of H_2Q , as is evidenced by an increase in the dark current. In our system, H_2Q is considered to act as a supersensitizer.¹²⁾ The electrode potential giving a maximum photocurrent (Fig. 3) was shifted anodically with the decrease in pH of the electrolyte solution. This may be due to the shifts of the flatband potential of SnO_2 as well as of the redox potential of H_2Q . Figure 4 shows the dependence of the maximum photocurrent on the pH of the electrolyte. The largest photocurrent was observed at pH around 4. Below pH 4, a chemical decomposition of Chl a in an acidic condition¹³⁾ is thought responsible for the photocurrent decrease. One of the possible causes for the photocurrent decrease above pH 4 might be the shift of the flatband potential of SnO_2 in a direction unfavorable for the electron injection from the excited Chl a molecules.

The quantum efficiency for photocurrent generation has been calculated on the basis of absorbance measurements for Chl a-stearic acid mixed monolayers at the SnO_2 /electrolyte interface. The results are listed in Table 1 together with the observed

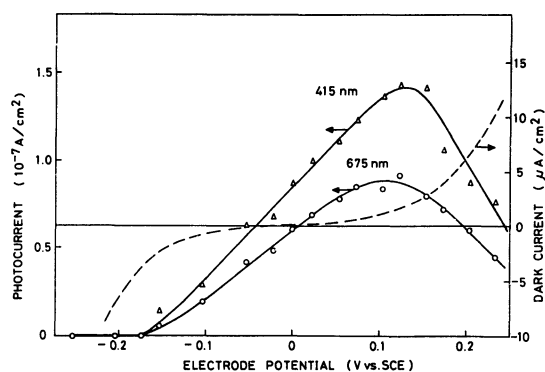


Fig. 3. Photocurrent-potential curves at Chl a monolayer electrode. Electrolyte, H_2Q 0.05 M, Na_2SO_4 0.1 M and phosphate buffer 0.025 M (pH 6.9). ---: The background dark current.

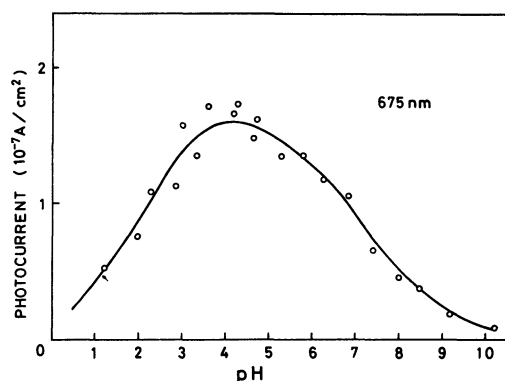


Fig. 4. pH dependence of the maximum photocurrent at Chl a monolayer electrode. Electrolyte, H_2Q 0.05 M and Na_2SO_4 0.1 M. The electrode potential is dependent on the pH value employed (see text).

Table 1. Photocurrent Quantum Efficiencies and Photovoltages
at Chl a-Stearic Acid (C₁₈) Mixed Monolayers

Chl <u>a</u> /C ₁₈ Molar ratio	Chl <u>a</u> surface concentration (10 ¹³ mole- cules/cm ²)	Quantum efficiency for photocurrent ^a (%)				Photovoltage ^b (mV)	
		pH 7		pH 4		Red max.	Blue max.
		Red	Blue	Red	Blue		
Chl <u>a</u> alone	10.0	2.7	4.0	4.3	6.4	- 8	-11
4/1	8.7	2.6	3.4	4.2	5.4	- 9	-14
2/1	8.0	5.6	7.3	9.0	11.7	-11	-16
1/1	7.4	7.6	9.8	12.2	15.7	-14	-18

^a At red peak (~675 nm) and blue peak (~415 nm) of the photocurrent;
electrode potential, +0.1 V (pH 7) and 0.3 V (pH 4) vs. SCE.

^b Incident photon flux was $1.4 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$; pH 7.

photovoltages. With increasing molar fraction of C₁₈, both the photocurrent quantum efficiency and photovoltage tend to increase. This phenomenon is supposedly due to an increase in the Chl a-Chl a intermolecular distance, because an increase in the intermolecular distance would result in a decrease in the Chl a-Chl a intermolecular energy transfer, which should necessarily accompany an energy loss within the monolayer. The sufficiently high quantum efficiency (12-16 %) observed here would permit an application of the present Chl monolayer/SnO₂ system as a useful *in vitro* model of the photosynthetic primary processes. Further detailed investigations are under way.

References and Notes

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