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PHOTOELECTROCHEMICAL STUDY OF CHLOROPHYLL-*a*-PVA COMPLEX FILM ON SnO_2 ELECTRODE

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Photoelectrochemical behavior of Chl-*a*(670) and Chl-*a*(740)-PVA complex films deposited on SnO_2 optically transparent electrode was investigated in an electrolyte solution containing hydroquinone as a reducing agent. For both films, the anodic photocurrent rose from -0.12 V or -0.13 V vs. SCE and reached a maximum at ca. +0.2 V. The spectrum of the photocurrent coincided with the absorption spectrum.

Recently, Honda et al.1, 2) reported the photoelectrochemical behavior of Chl-*a* monolayer or multilayers deposited on an SnO_2 optically transparent electrode (OTE). They observed the prominent anodic photocurrent when hydroquinone was added to the electrolyte solution. We3, 4) prepared the chlorophyll/water-soluble macromolecular complexes using polyvinyl alcohol(PVA), polyvinylpyrrolidone(PVP), polyethylene glycol(PEG) and bovine serum albumin(BSA), as an artificial model compound of the chlorophyll-protein complex *in vivo*. Among these polymers, PVA swells but not dissolves in water at room temperature. Therefore Chl-*a*-PVA complex is most effective in making electrodes for the photoelectrochemical study in electrolyte solution.5) We have investigated in the present work the photoelectrochemical behavior of the Chl-*a*-PVA complex film, in which Chl-*a* assumes a species of Chl-*a*(670) or Chl-*a*(740), deposited on SnO_2 OTE in the electrolyte solution containing hydroquinone(H_2Q) as a reducing agent.

Chl-*a* was isolated from fresh spinach leaves.4) Polyvinyl alcohol(PVA); PVA-EC: molecular weight 77000, degree of saponification, 99.9 mol-%, was kindly donated by Kuraray Co. Ltd. PVA was purified by reprecipitating in water-methanol. As the substrate for Chl-*a*-PVA complex film, SnO_2 OTE (Matsuzaki Shinku Ltd.) was used. The electrode was 10 x 10 cm in size with one side being coated with SnO_2 layer, 2000 Å thick. The SnO_2 layer had a specific resistance of 4×10^{-3} Ω·cm and an optical transmittance of 80-90% in the visible region above 400 nm.

Chl-*a*-PVA complex was prepared according to the preparation method (A) of chlorophyll/water-soluble macromolecular complexes.6) That is, Chl-*a*/PVA/organic solvent/water solution, the composition of which is shown in Table 1, was spread uniformly on the surface of an SnO_2 OTE glass plate and dried in an air atmosphere, giving the Chl-*a*-PVA complex film. The Chl-*a*-PVA complex film deposited on an SnO_2 OTE, thus prepared, was used for the photoelectrochemical measurements.

The electrochemical setup for photocurrent measurements is essentially the same as that reported by Honda et al.[1)] The Chl-*a* complex film-deposited SnO_2 electrode was mounted as a bottom of the cell(capacity, 100 ml) to give 12.6 cm^2 as the available area for electrolysis. The supporting electrolyte was 0.1 M (1 M = 1 mol dm^{-3}) Na_2SO_4, and during all the experiments the solution was flushed with commercial purity N_2 gas. The electrolyte solution contained 0.05 M H_2Q as a reducing agent and 0.025 M phosphate buffer (pH 6.9). The potential of the SnO_2 electrode was controlled by means of a Hokuto Denko potentiostat, Model HA-201, where a platinum plate and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. As the light source, a projector lamp (Kondo Electrical Industrial Co.; KP-10SE, 100 V, 300 W) was used in combination with a color filter (Toshiba Kasei, L-42, which eliminates light below 420 nm) to eliminate photoresponse of SnO_2, or in combination with a band-path filter (half value breadth, 10 nm: Toshiba Kasei Ltd.) to obtain the photocurrent spectrum. Photocurrents were measured at room temperature with a Toa Electronics, DC microvolt-ammeter, Model PM-18R.

Table 1. Chl-*a*-PVA complex films used for the photoelectrochemical measurements

Complex	Composition of raw materials[a)]				Characteristics of Chl-*a*-PVA complex film				
	Chl-*a* (μg)	PVA (mg)	org. solv. (ml)	water (ml)	Chl/PVA[b)]	red peak (nm)	PVA (mg cm^{-2})	Chl-*a* (μg cm^{-2})	thickness[c)] (μm)
Chl-*a*(670)-PVA	1090	272	EtOH 0.3 +MeOH 0.1	2.5	0.34	675	11	43.6	80
Chl-*a*(740)-PVA	1070	95	acetone 0.3	2.2	0.97	735(+670)	3.8	42.8	25

a) The raw material was spread on the OTE electrode surface of 25 cm^2.
b) Molar ratio, Chl-*a*/PVA. c) In dry condition.

Table 1 shows the raw materials and characteristics of Chl-*a*(670) and Chl-*a*(740)-PVA complex films. It is generally considered that the Chl-*a*(670) is a monomeric Chl-*a* species and the Chl-*a*(740) is a microcrystalline $(\text{Chl-}a\cdot 2H_2O)_n$ species.[4)]

Figures 1 and 2 show the action spectra of the anodic photocurrent for the Chl-*a*(670) and Chl-*a*(740)-PVA complex films on SnO_2 OTE, together with their absorption spectra at the SnO_2-air interface. The absorption peaks of Chl-*a*(670)-PVA complex film lie at 440 and 675 nm with the peak intensity ratio of 1.7 : 1. The peaks of Chl-*a*(740)-PVA complex film lie at 445, 670, and 735 nm with the ratio of 0.93 : 0.43 : 1. These features of absorption spectra almost exactly correspond to those for the aqueous Chl-*a*(670) and Chl-*a*(740)-PVA complex solutions.[4)] In the action spectrum for Chl-*a*(670)-PVA complex film, the peak wavelengths are situated at 427 and 678 nm with the peak intensity ratio of 2.2 : 1, and for Chl-*a*(740)-PVA complex film, 427, 680, and 736 nm with the ratio of 2.4 : 1.6 : 1. Thus, the action spectra of both complex films coincide well with the corresponding absorption spectra, except for the peak intensity ratio. The ratio is higher in the action spectrum than in the absorption spectrum, which was also found in photoelectrochemical behavior of Chl-*a* monolayer or multilayers on SnO_2 OTE.[1, 2)] These results suggest that the anodic photocurrents observed in the Chl-*a*(670) and Chl-*a*(740)-PVA complex films on SnO_2 OTE correspond to an electron

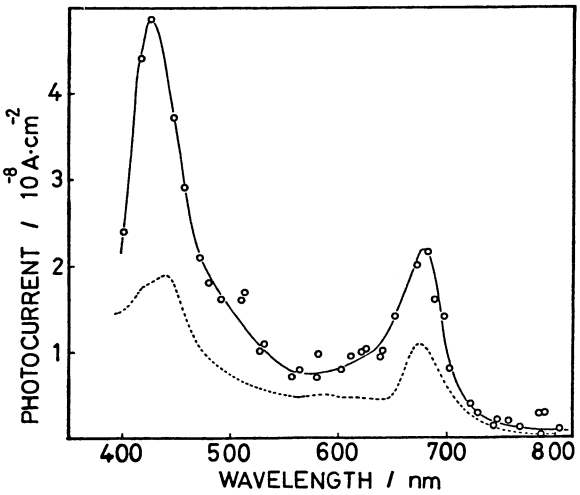

Fig. 1. Action spectrum for the anodic photocurrent at Chl-*a*(670)-PVA complex film on SnO_2 OTE. Electrolyte composition was 0.1 M Na_2SO_4 + 0.05 M H_2Q + 0.025 M phosphate buffer(pH 6.9). Electrode potential, +0.015 vs. SCE. Light intensity, 1.2 J/m^2. The broken curve is the absorption spectrum (arbitrary unit).

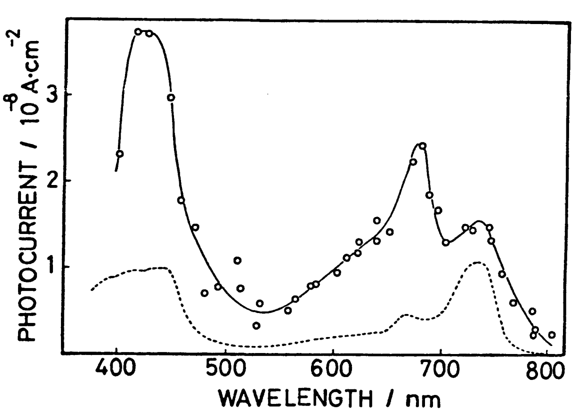

Fig. 2. Action spectrum for the anodic photocurrent at Chl-*a*(740)-PVA complex film on SnO_2 OTE. Electrolyte composition and other conditions are the same as in Fig. 1. The broken curve is the absorption spectrum (arbitrary unit).

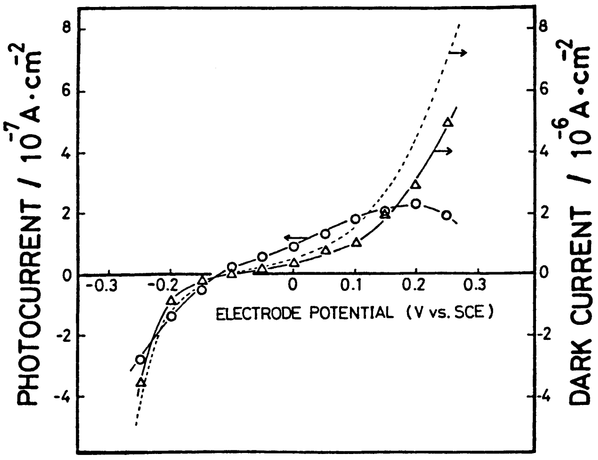

Fig. 3. Photocurrent-potential curve at Chl-*a*(670)-PVA complex film on SnO_2 OTE. Electrolyte composition was 0.1 M Na_2SO_4 + 0.05 M H_2Q + 0.025 M phosphate buffer(pH 6.9). Light intensity, 1.0 x 10^3 J/m^2. (—△—): the dark current values corrected for the blank dark current at the PVA film on SnO_2 OTE, (- - - - -): the dark current not corrected.

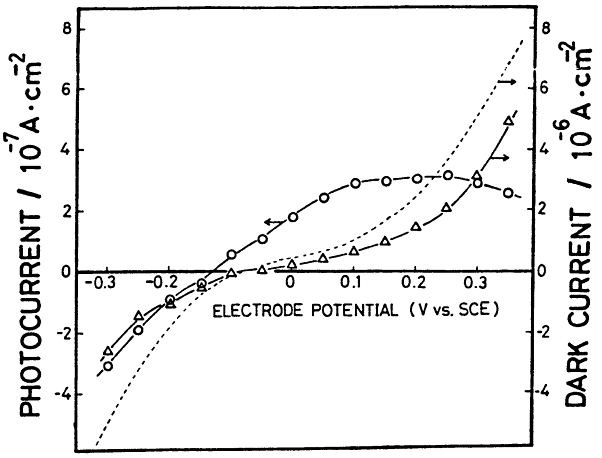

Fig. 4. Photocurrent-potential curve at Chl-*a*(740)-PVA complex film on SnO_2 OTE. The experimental condition is the same as in Fig. 3. The dark currents are also shown.

transfer from the excited Chl-*a* molecules to the conduction band of SnO_2. It is interesting that the incident light with a shorter wavelength produced more effectively a photocurrent, and its cause will be elucidated in future.

Figures 3 and 4 show the photocurrent-potential curves for the Chl-*a*(670) and Chl-*a*(740)-PVA complex films on SnO_2 OTE. The small blank photocurrent was observed at the PVA film alone with the corresponding density (mg cm^{-2}) deposited on SnO_2 OTE. This photocurrent was a little greater than that observed at SnO_2 OTE and may be due to the excitation of both SnO_2 and a trace of contaminant in PVA film. A correction for the blank photocurrent was performed by subtracting it from the photocurrent observed at Chl-*a*-PVA complex film on SnO_2 OTE. The corrected photocurrent values are presented in Figs. 3 and 4, together with the dark currents.

For the Chl-*a*(670) and Chl-*a*(740)-PVA complex films, the anodic photocurrents rise from -0.12 and -0.13 V vs. SCE, respectively, and they increase up to maxima at ca. +0.2 V and then gradually decrease. Such electrode potential dependences are consistent with those reported by Honda et al.$^{1)}$; the anodic photocurrent due to Chl-*a* excitation rises at -0.17 V vs. SCE and reaches a maximum at ca. +0.1 V for Chl-*a* monolayer on SnO_2 OTE. The cathodic photocurrents with higher cathodic electrode potential for both films, may be ascribed to a photochemical oxidation of excited Chl-*a* by O_2 followed by an electron transfer from the conduction band of SnO_2 by tunneling because bubbling of the electrolyte solution was done with N_2 gas of commercial purity without further purification.$^{2)}$ The difference of Chl-*a* species in the complex, namely Chl-*a*(670) or Chl-*a*(740), has only a small effect on the phtocurrent-potential characteristics. Also, it does not appear to have a great effect on the photoconversion efficiency because the Chl-*a*/PVA molar ratio of Chl-*a*(740)-PVA complex is higher by a ratio of 2.9 than that of Chl-*a*(670)-PVA complex as shown in Table 1.

It is concluded that the anodic photocurrents for both Chl-*a*(670) and Chl-*a*(740)-PVA complex films are due to Chl-*a* excitation by incident light energy with the effective electron donor of H_2Q, and that the mechanism of electron transfer in the present system may be the same as that proposed by Honda et al.$^{1)}$ The Chl-*a*-PVA complex film has the advantage that it is easy to prepare in a laboratory and that it can be used as the electrode for a long time without decomposition of Chl-*a* species since a Chl-*a* molecule in complex with PVA is stabilized against even strong light radiation. Finally we stress that the present system will become very useful for an *in vitro* simulation of photosynthetic primary processes by introducing various interesting biological materials into the system.

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