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A NOVEL TRANSFORMATION OF CHLOROPHYLL a AGGREGATES IN POLY(VINYL ACETATE) FILMS BY IMMERSING INTO WATER. OBSERVATION OF POSITIVE OR NEGATIVE PHOTO-INDUCED POTENTIAL SHIFTS FOR THE RESULTED FILMS COATED ON PLATINUM ELECTRODE

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Upon immersing into water, the chlorophyll a(chl a)/poly vinyl acetate) film cast from dioxane or dimethyl sulfoxide (DMSO) showed a transformation from chl a-dioxane aggregate (692 nm) to monomeric(668 nm) or from chl a-DMSO aggregate(695 nm) to (chl a$\cdot 2H_2O)_n$(746 nm), respectively. The platinum electrodes coated by the two types of transformed films showed the opposite direction of photo-induced potential shift.

A considerable amount of work on aggregation of chlorophyll a(chl a) *in vitro* has been published and reviewed.1) We have recently described the preparation and spectral properties of a new kind of aggregates of chl a using the system of water soluble macromolecules or dimethyl sulfoxide(DMSO).2) It has been noted that the kind of chl a aggregate affects on the power conversion efficiency of chl a photovoltaic cells; 10 times higher value has been found for hydrated microcrystalline form (chl a$\cdot 2H_2O)_n$ than for anhydrous monomeric form.3) Aizawa et al.4) have observed the opposite photo-induced potential shift for the platinum electrodes coated by the thin layer of such liquid crystals as N-(p-methoxybenzylidene)-p-butylaniline(MBBA) and 4'-heptyl-4-cyanobiphenyl(HCB) containing magnesium chlorophyll a(Mg-chl a) or manganese chlorophyll a(Mn-chl a); Mg-chl a/MBBA electrode gave the positive photo-induced potential shift but Mn-chl a/HCB electrode gave the negative shift. Recently, Inamura et al.5) have reported the photoelectrochemical behavior of chl a(670)- and chl a(740)- poly(vinyl alcohol) complex films coated on SnO_2 electrode but they have observed same direction of photocurrent (anodic) for both films because chl a acts only as a sensitizer of SnO_2 as Honda et al.6) pointed out.

In the present paper, we would like to report a novel transformation of chl a aggregate in poly(vinyl acetate)(PVAc) film cast from dioxane or DMSO leading to either anhydrated monomeric form or hydrated microcrystalline form by immersing into water. It is quite interesting to note that the two kind of resulted films on platinum electrodes show the opposite direction of photovoltage upon irradiation of light. Positive photo-induced potential shift was developed by the monomeric chl a/PVAc electrode. In sharp contrast, hydrated polycrystalline chl a/PVAc electrode gave the negative photo-induced potential shift.

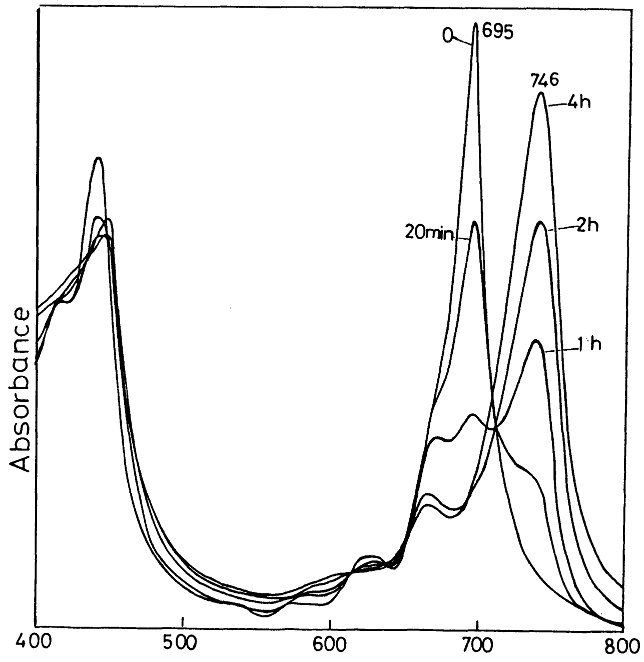

Fig. 1. Time dependent spectral change of PVAc/chl a-DMSO film caused by immersing into water.

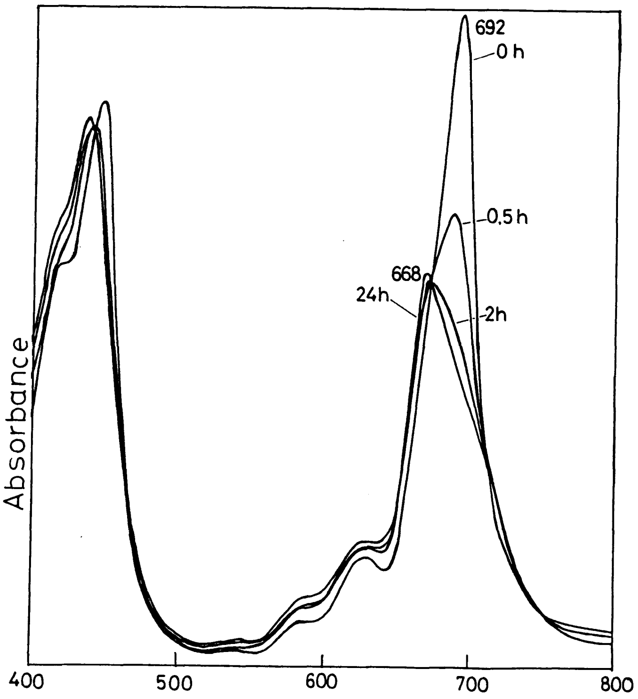

Fig. 2. Time dependent spectral change of PVAc/chl a-dioxane film caused by immersing into water.

Chl a was isolated from fresh spinach leaves and its purity was checked by HPLC analysis.[7)] PVAc was prepared by the radical polymerization of vinyl acetate initiated by benzoyl peroxide (molecular weight, 172000). DMSO and dioxane were GR grade reagents furnished by Wako Pure Chemical Industries Ltd. PVAc/chl a-DMSO film was cast on the surface of glass plate or platinum electrode from DMSO solution of PVAc and chl a (weight ratio, 3:1 ; chl a concentration, 25 nmol/cm^2) in a calcium chloride desiccator *in vacuo*. PVAc/chl a-dioxane film was cast from dioxane solution of PVAc and chl a in an oven desiccator at 40 °C.

The absorption spectra of the films cast on the glass plate were recorded on a Shimadzu UV-200 spectrophotometer. As shown in Fig. 1, PVAc/chl a-DMSO film had a sharp absorption peak at 695 nm. It was closely corresponded to the spectrum of the chl a aggregate formed in 70% DMSO solution (DMSO:H_2O=70:30, v/v) as we have already reported in a previous paper.[2b)] On the other hand, PVAc/chl a-dioxane film had an absorption maximum at 692 nm as shown in Fig. 2. It seemed to correspond with the spectrum of chl a-dioxane complex which had been reported by Iriyama et al.[8)]

The films cast on the glass plate were immersed into an aqueous phosphate buffer solution (pH 6.98; 25 °C) and the absorption spectra at differnt stages of transformation were recorded. Upon immersing, PVAc/chl a-DMSO film shifted the absorption peak from 695 to 746 nm, whereas PVAc/chl a-dioxane film did from 692 to 688 nm. It may be considered that the 688 nm form is a monomeric chl a species and the 746 nm form is a hydrated microcrystalline (chl a$\cdot 2H_2O)_n$ species.[1c,1d)]

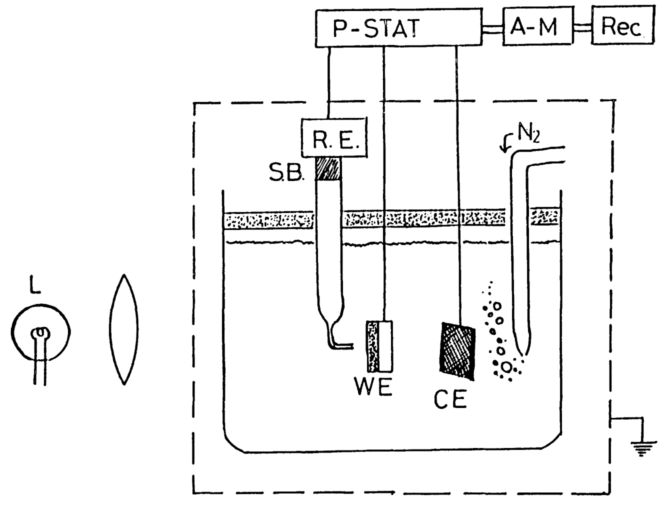

Fig. 3. The electrochemical setup for photovoltage measurements.

WE: Working Electrode (PVAc-chl a/Pt)
CE: Counter Electrode (Platinized Pt)
SB: Salt Bridge
P-STAT: Potentiostat
A-M: Ammeter
Rec: Recorder
L: Light Source

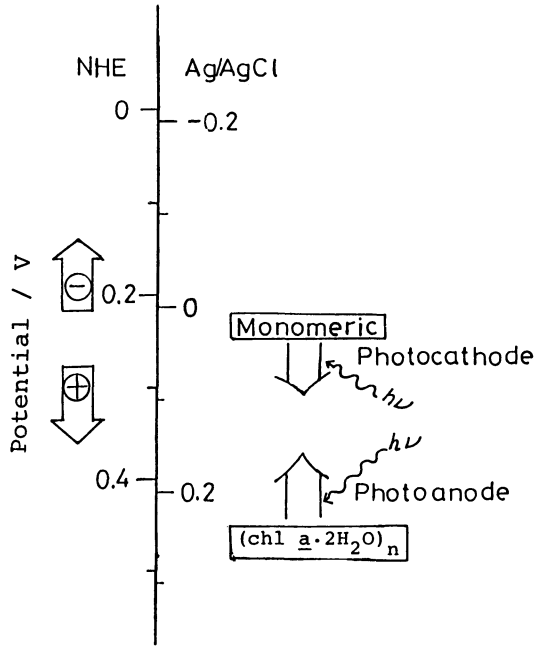

Fig. 4. The direction of potential shift of the electrode on irradiation of light.

The PVAc/chl a-DMSO or PVAc/chl a-dioxane film deposited on the platinum electrode also should transform from chl a-DMSO aggregate to (chl a$\cdot$2H$_2$O)$_n$ or from chl a-dioxane aggregate to monomeric form, respectively, upon immersing into water, as with the films deposited on the glass plate.

The electrochemical setup for photovoltage and photocurrent measurements is shown in Fig. 3. The electrolyte solution contains 0.067 M phosphate buffer (pH 6.98). The potential of the PVAc/chl a-coated platinum electrode was measured and controlled by means of a Hokuto HA-301 potentiostat/galvanostat, where platinized platinum electrode and Ag/AgCl electrode were served as the counter electrode and the reference electrode, respectively. Light was provided by a 300 W tungsten projector lump with filters, Toshiba VR-61 and IRQ-80. The PVAc/(chl a$\cdot$2H$_2$O)$_n$-coated platinum electrode resulted by immersing the PVAc/chl a-DMSO film into water showed a dark potential at 260±30 mV vs. Ag/AgCl, and showed a negative potential shift to 220±30 mV upon irradiation of light. On the other hand, the resulted PVAc/monomeric chl a coated platinum electrode from chl a-dioxane film showed a dark potential at 40±30 mV vs. Ag/AgCl and showed a positive potential shift to 70± 30 mV upon irradiation of light. Table 1 shows an example of data for each electrode (additional three runs for each experiments, not shown). Although the electrode reactions are not clarified, the direction of the potential shift is opposite with each other. Detailed studies are now in progress. Figure 4 shows a schematic representation of the direction of potential shift for the transformed PVAc/chl a coated on platinum electrode upon irradiation of light.

Table 1. The dark potentials, photopotentials, and photovoltages for the transformed PVAc/chl a films coated on the platinum electrode.

Electrode	(Casting solvent)	Dark potential mV vs. Ag/AgCl	Photopotential mV vs. Ag/AgCl	Photovoltage mV
PVAc/(chl a·$2H_2O)_n$	(DMSO)	273	203	-70 (anodic)
PVAc/monomeric chl a	(dioxane)	62	97	+35 (cathodic)

A positive potential shift of the platinum electrode coated by monomeric chl a has been reported for chl a-lipid multilayer[9)] and the thin layer of liquid crystal such as chl a/MBBA.[4)] However, no negative potential shift on irradiation of light has been reported for the platinum electrode coated with any form of chl a. Present study gives a new method to prepare a photocathodic and photoanodic polymer electrodes with different chl a form. We have found that chl a molecules in PVAc film was stabilized much better than in poly(vinyl alcohol) film reported by Inamura et al.,[5)] however, it was gradually decomposed to degradation products by prolonged irradiation of light.

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