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Photoelectrochemical Behavior of Chlorophyll a-Lipid Films on a Platinum Electrode in an Aqueous Electrolyte

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The photoelectrochemical behavior of chlorophyll a-lipid mixed monolayers coated on a platinum electrode by the Langmuir-Blodgett technique was investigated under potentiostatic conditions in an aqueous electrolyte in the absence of redox agents. Under illumination, cathodic photocurrents were observed at electrodes coated with a sufficient number of monolayers. The quantum efficiency of the photocurrent was estimated to be about 10^{-4}, much lower than that obtainable for dye-sensitized photocurrent on semiconductor electrode. The cathodic photocurrent increased with lowering in the pH of electrolyte. The possibility of the photoreduction of water by excited triplet chlorophyll a is discussed on the basis of observed pH dependence and correlation of the redox potentials involved.

During the last decade an increasing number of studies have appeared on the photoelectrical and photoelectrochemical behavior of chlorophyll (Chl) in the form of solid layers coated on metal electrodes.[1—13] The photoconductive nature of solid Chl films in various forms, such as amorphous layers,[1,3,5] microcrystals,[2,4,5] and monolayer assemblies,[6,7] in contact with metal substrates has been established by the use of metal/Chl/metal sandwich-type photovoltaic cells. However, the organic semiconductivity inherent to solid-state Chl, postulated for the microcrystalline films[2,14] in order to explain the photoelectrical rectifying effects at metal/Chl contacts, is the subject of controversy;[4,15] in particular, it seems unlikely for the monolayer assemblies.[6,16,17] In photoelectrochemical cells employing metal electrodes (mostly platinum) coated with various forms of Chl films,[8—13] cathodic photocurrents have usually been obtained, presumably reflecting the *p*-type semiconduction formed within a bulk Chl layer. Water splitting reactions with use of Chl-coated platinum photocathodes have been demonstrated by several groups.[10,13] Such behavior is in contrast to the case of Chl-coated *n*-type semiconductor electrodes which produce anodic sensitized photocurrents.[18,19]

According to the principles of dye sensitization processes, the photocurrent of dye molecules adsorbed on a metal electrode should be incomparably less efficient than that obtained at a semiconductor electrode, owing mainly to the rapid energy quenching of dye excited states by free electrons in the metal, as reported by Memming[20] and Gerischer and Williug.[21] Ample efficiency for dye-sensitized photocurrent on a metal electrode could thus be expected in cases where the dye layer is thick enough to develop the bulk effects such as *p*-type photoconductivity. Typical of this case are solid films of metal phthalocyanines[22] and porphyrins[23] which are regarded as *p*-type organic semiconductors.

Reports have been given on the anodic sensitized photocurrents obtained for various monolayer assemblies (Langmuir-Blodgett films) of Chl coated on an SnO_2 semiconductor electrode,[19,24—26] where quantum efficiency of the photocurrent was investigated as a function of the surface concentration of Chl[19,24] and thickness of the monolayers.[25] For such a Chl-sensitized semiconductor photoanode, it was confirmed that the single monolayer film of Chl that is amply diluted in the surface concentration gives the highest quantum efficiency (≤ 0.25) for photocurrent generation.[26]

By means of the Langmuir-Blodgett technique which allows a precise and uniform control of the film thickness, we have investigated the photocurrent behavior at the thin monolayer assemblies of a Chl-lipid mixture on a platinum electrode. The behavior observed in this system, such as photocurrent-potential characteristics, pH dependence of photocurrent, and effect of the film thickness was found to be in contrast to the corresponding observations in a Chl multilayer/semiconductor system.[25]

Experimental

Pure Chl a was obtained from spinach leaves in the usual manner.[19] L-α-Dipalmitoyllectithin (DPL from Sigma Chemical.) was employed as a two-dimensional diluent for a Chl a monolayer,[24] in order to keep Chl a from possible photodegradation[27] as well as to suppress the energy dissipation within layers due to the concentration quenching characteristic of Chl a molecules.[28] A monomolecular layer consisting of Chl a and DPL at molar ratio 1/1 was prepared, using benzene as a spreading solvent, on an aqueous phosphate buffer (pH$\approx$ 8) in a Langmuir trough. The monolayers were then deposited on the surface of a platinum electrode substrate (0.05 mm thick, 2.5×2.5 cm^2), which had been treated with several organic solvents and hot sulfuric acid to make the surface hydrophilic, by serial dipping of the substrate across the supernatant monolayer under a surface pressure of 20 dyn cm^{-1} (1 dyn$=10^{-5}$ N); each monolayer coated on the substrate was vacuum-dried prior to the subsequent deposition. The deposition ratio for the Chl a–DPL mixed monolayer with respect to the platinum surface area was 0.7—1.0, indicating that the film was packed less densely on the electrode than on the water.[29]

Sodium sulfate (reagent grade) dissolved in doubly distilled water, 0.1 M (1 M$=$1 mol dm^{-3}), was used as a neutral electrolyte except when H_2SO_4 and/or NaOH was added for pH variation. The electrolyte solution was flushed with nitrogen which had been deoxygenated by passing over an activated copper column. The electrochemical cell employed was of one compartment including three electrodes; the potential of the Chl a–DPL film-coated platinum electrode was regulated with a Hokuto Denko Model HA-101 potentiostat, using a saturated calomel electrode (SCE) and a platinum wire as a reference electrode and a counterelectrode, respectively. Photo- and dark currents were measured on a Keithley Model 610 B picoammeter. The light source was a 500-W Xe arc lamp in combination with a grating monochromator. The observed photocurrents were corrected for incident photon flux, corresponding to *ca.* 1.2×10^{16} photons s^{-1}. For details of the experimental setup as well as the monolayer deposition technique, refer to the previous paper.[19]

Results and Discussion

Photocurrent Characteristics. When a single Chl a-DPL monolayer on the platinum electrode was illuminated, almost no significant photocurrent was observed. This can be ascribed to the rapid energy-quenching of excited Chl a by free electrons in the metal[20,21] as well as to a reversible and simultaneous exchange of electrons *via* the metal/Chl a interface (no rectifying property). The former phenomenon, mainly responsible for the minimal photocurrent, has been elucidated by Kuhn[30] on the basis of fluorimetric studies.

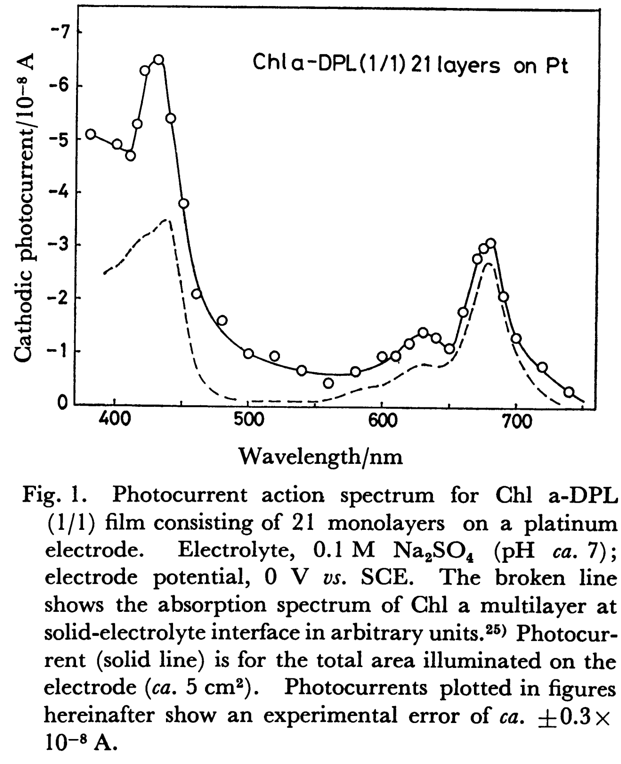

Fig. 1. Photocurrent action spectrum for Chl a-DPL (1/1) film consisting of 21 monolayers on a platinum electrode. Electrolyte, 0.1 M Na_2SO_4 (pH *ca.* 7); electrode potential, 0 V *vs.* SCE. The broken line shows the absorption spectrum of Chl a multilayer at solid-electrolyte interface in arbitrary units.[25] Photocurrent (solid line) is for the total area illuminated on the electrode (*ca.* 5 cm^2). Photocurrents plotted in figures hereinafter show an experimental error of *ca.* $\pm0.3\times10^{-8}$ A.

Electrodes coated with more than several monolayers were found to develop significant cathodic photocurrents upon illumination. Figure 1 shows the photocurrent action spectrum obtained for a film consisting of 21 monolayers with an absorption spectrum of a pure Chl a multilayer[25] for comparison. Apparently the cathodic photoresponse follows the absorption of Chl a, showing peaks at around 680 nm and 430 nm in the red and blue bands, respectively. The observed action spectrum suggests that the monomeric form of Chl a is the main species participating in the present photoelectrochemical reaction. No significant changes due to the formation and photochemical involvement of the hydrated Chl species absorbing in the far-red region (≈740 nm)[2,4,5,12,13] was detected, at least not in the action spectrum.

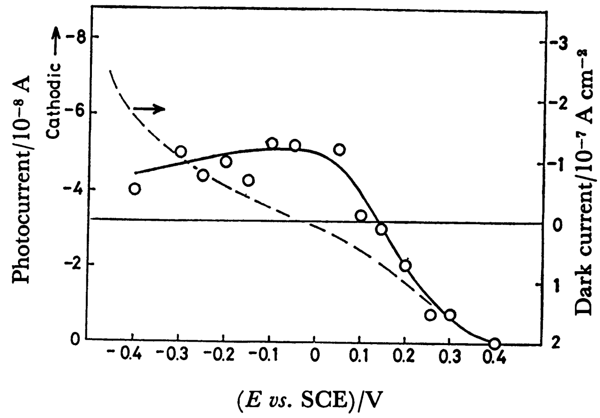

Fig. 2. Photocurrent-potential characteristics. —○—: Photocurrent, ----: dark current. Illumination at 675 nm. Film and electrolyte composition are the same as in Fig. 1.

Figure 2 shows the dependence of the photocurrent on electrode potential. Cathodic photocurrent, *i.e.*, electron injection from the Pt/Chl a electrode to the solution, occurred at potentials more negative (cathodic) than +0.4 V *vs.* SCE, increasing with cathodic polarization until it became saturated at around 0 V.

Generation of cathodic photocurrent can be interpreted schematically in terms of the electron donation from excited Chl a molecules at the film-electrolyte interface to some reducible species (A) in the electrolyte and the subsequent reduction of the produced Chl a cation radical by free electrons of the electrode, namely,

$$\text{Chl a} \xrightarrow{h\nu} \text{Chl a}^* \tag{1}$$

$$\text{Chl a}^* + \text{A} \longrightarrow \text{Chl a}^{\dagger} + \text{A}^{\text{-}} \tag{2}$$

$$\text{Chl a}^{\dagger} + e^-_{\text{Pt}} \longrightarrow \text{Chl a.} \tag{3}$$

Such a mechanism is substantially the same as that proposed for an electron transfer process involved in dye sensitization on a *p*-type semiconductor photocathode.[31] The above reaction, however, hardly proceeds if the dye layer on a metal is not as thick as several monolayers, because of the quenching phenomenon as well as the absence of rectifying properties. This differs from the case of semiconductor electrode surface where only monolayer-thick adsorption of dye is sufficient to develop a considerable efficiency of photocurrent. In the semiconductor electrode, electron flow is rectified *via* the space charge layer in which energy transferred from the dye, if any, can be utilized for charge separation which leads to photocurrent generation. If, however, the dye layer on a metal is of sufficient thickness, the photooxidation of Chl a with an acceptor in solution (Eq. 2) can take place at the film/electrolyte interface where the quenching of excited dye by the metal can be suppressed by the spatial separation of its interface from the metal surface. The photooxidized Chl a may subsequently be reduced by electrons which migrate from the metal surface by hopping through the dye layer. Another reaction mechanism, applicable to the *p*-type semiconductor/dye interface, which involves the direct reduction of excited-state Chl a by electrode at the metal/film interface ($\text{Chl a}^* + e^-_{\text{Pt}} \rightarrow$

Chl $\mathrm{a}^{\overset{\cdot}{-}}$) is unlikely since reoxidation of Chl $\mathrm{a}^{\overset{\cdot}{-}}$ into Chl a would occur simultaneously at the metal surface.

The proposed mechanism is compatible with the fact that the onset potential for the cathodic photocurrent, 0.4 V *vs.* SCE, was observed at a somewhat more negative potential than the oxidation potential of the ground state Chl a, *ca.* 0.54 V *vs.* SCE,[32] since the reaction process of reducing Chl a cation radical (Eq. 3) is expected to be promoted at potentials $<$*ca.* 0.54 V on an electrochemical basis. According to the mechanism, the observed onset potential further implies that the oxidation potential of Chl a, which has so far been estimated in nonaqueous media on account of the insolubility of Chl, would be situated at $\geq$0.4 V *vs.* SCE in the monolayer assembly in contact with an aqueous electrolyte.

In the present system, semiconduction in the solid Chl film is not important to explain the observed photoeffect because the monolayer assemblies of Chl are generally not regarded as good semiconductor materials,[16,17] unlike the amorphous or microcrystalline films which display significant photoconductivity.[1,2,5] It should be noted that the Chl a monolayers studied here were doped with lipid molecules which diminish the Chl–Chl electronic interaction needed for the developing of photoconduction.

A blank test was carried out by irradiating a platinum electrode free of Chl a with 680 nm and 430 nm light. No photocurrent was detected at electrode potentials below +0.4 V *vs.* SCE. A slight anodic photocurrent was detectable under 430 nm irradiation at *ca.* 0.4 V, but this intrinsic photoresponse of platinum was within experimental error and is negligible.

Effect of Film Thickness. The magnitudes of the cathodic photocurrents for various numbers of layers on the platinum were compared at an applied elecrode potential of 0 V *vs.* SCE where the photocurrent tends to be saturated (Fig. 2). The results are summarized in Fig. 3.

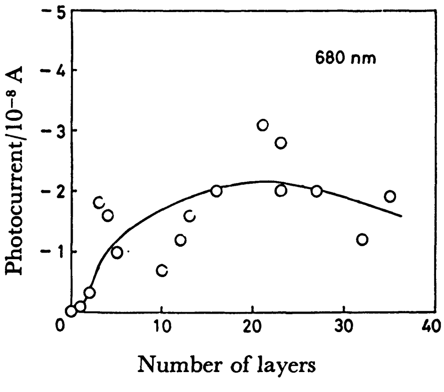

Fig. 3. Relation between cathodic photocurrent and the number of layers deposited on the platinum electrode. Illumination at 680 nm. Electrolyte, 0.1 M Na_2SO_4; electrode potential, 0 V *vs.* SCE.

No significant photocurrent was observed with a single monolayer film. Photocurrent, however, increased with an increase in the number of layers (*i.e.*, total film thickness), reaching a maximum at 20—30 layers. The increase may result from the spatial separation of the film/solution interface participating in the photooxidation reaction of Chl a with an acceptor in the electrolyte (Eq. 2) from the metal/film interface involved in the dark electron transfer (Eq. 3). Such a separation of the two interfaces by stacking a sufficient number of monolayers would thus suppress the energy dissipation of dye excited at the film/electrolyte interface due to energy transfer as well as back electron transfer[33] toward the metal. The observed saturation of photocurrent above 20 layers may be due to the increased electrical resistance within the film.

The quantum yields of steady state cathodic photocurrents obtained for 20—30 layers, estimated taking into account the surface reflectance of platinum (*ca.* 0.7) with respect to incident light, are of the order 10^{-4} electron/photon. This is incomparably lower than the value, 10^{-1} electron/photon, reported for dye-sensitized cathodic photocurrents at a *p*-type semiconductor.[31] Such a low efficiency is apparently due to the minimal rectifying properties of the metal electrode. Using platinum electrodes coated with microcrystalline Chl a aggregates, Fong and co-workers have reported relatively efficient cathodic photocurrents[12] and claimed evidence for water splitting reaction.[13] However, it is presumed that the electrodes used in their system, prepared by drastic treatments of the surface Chl a layers with repeated platinizations,[13] may involve a certain photocatalytic effect ascribed to some Chl a-Pt composite and the observed phenomena cannot be attributed simply to the light reaction of Chl aggregate itself.

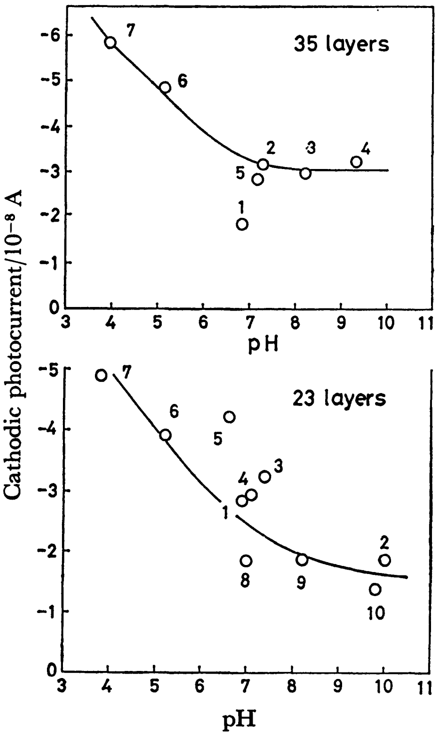

Fig. 4. Dependence of cathodic photocurrent on electrolyte pH. 35 layers and 23 layers on the platinum were examined under the same experimental conditions as in Fig. 3. The numbers on the plots stand for the experimental sequence.

Effect of pH on Photocurrent. The pH dependence of the photocurrent was investigated in order to clarify the nature of acceptor species involved in the photooxidation reaction of Chl a. Figure 4 shows the results obtained for films of 23 and 35 monolayers under a constant electrode potential of 0 V *vs.* SCE. In both cases, cathodic photocurrents tend to increase with lowering in pH. The increase occurs at pH's $<$*ca.* 7. Since the redox potential of Chl a can be regarded as almost independent of pH, the behavior clearly indicates that some protonic oxidant in the solution acts as an electron acceptor for excited Chl a. After a series of pH variation, an attempt was made to check the chemical degradation of Chl a by dissolving the illuminated samples in benzene. No significant change assigned to decomposed Chl a species, such as pheophytin, could be detected in the absorption spectrum, indicating that the chemical changes in Chl a during the course of pH variation is almost negligible.

In order to discuss the photooxidation reaction of Chl a with an acceptor, involvement of two donor states of Chl a, excited singlet and excited triplet states, should first be taken into account. It is known that the photoionization of Chl a by reaction with a redox agent in solution takes place exclusively *via* the excited triplet state, a long-lived species with a lifetime of *ca.* 2 ms.[34) A variety of oxidants[35) has thus far been found to react with the triplet state of Chl a producing Chl a radical cations. Using photovoltaic cells, Janzen and Bolton[6) found a large contribution of triplet state Chl a to the reduction of acceptor species immobilized in monolayer assemblies. Consequently, it is reasonable to assume that in the present system the photooxidation of Chl a (Eq. 2) takes place *via* the triplet state, from the viewpoint that an amply long lifetime of the excited state is needed to achieve the reaction with a dilute oxidant diffusing from the bulk of solution.

If we assume that the electrolyte used contains no impurities that can act as electron acceptors, water (proton) is the only possible oxidant involved because it can be reduced on an energetic basis by both the singlet and triplet excited states of Chl a which have oxidation potentials of -1.31 V and -0.79 V *vs.* SCE,[32) respectively. Here, the oxidation potential of the triplet state Chl a, the predominant species involved in the photooxidation process, is situated somewhat negative of the reduction potential of water at pH 7, namely -0.66 V *vs.* SCE. This suggests that the triplet Chl a cannot reduce water very efficiently in neutral solutions because of a rather small free energy change (overpotential). Since the lowering of pH brings about a positive shift in water redox potential which facilitates the reaction of triplet Chl a with a proton, the observed increase in photocurrent at pH's below 7 might result from the reduction of water by the excited triplet Chl a.

In contrast with the result shown in Fig. 4, the reverse behavior in pH dependence has been obtained with a Chl a multilayer-coated SnO_2 *photoanode*[25) using a similar electrolyte to that of the present system. Anodic sensitized photocurrent of Chl a observed was found to increase at pH's higher than 7. This was rationalized by the recognition that the oxidation potential of ground state Chl a, 0.54 V *vs.* SCE, is in the vicinity of the water oxidation potential at pH 7, 0.57 V *vs.* SCE, and the reduction by water of the Chl a cation radical produced by electron injection into SnO_2 is promoted by increasing of pH (*i.e.*, a negative shift in water oxidation potential).

The combination of both features of Chl a *photoanode* and *photocathode* in pH dependence brings us to the view that the oxidation and reduction of water by *in vitro* photoexcited Chl a, or at least by monomeric Chl a, would be difficult in *neutral* aqueous solutions owing to the absence of any overpotential (*i.e.*, free energy change) sufficient for an electron transfer reaction. Watanabe and Honda[36) have recently found that Chl a cation radical produced by electrolysis, which corresponds to the photooxidized form of Chl a produced at the photoanode, has an extremely low rate constant for the reaction with water in an organic solution, suggesting that the oxidation of water by excited Chl a is inefficient. Consequently, photosplitting of water by *in vitro* Chl a is thought to be feasible under either acidic or alkaline conditions which can promote, respectively, the photoreduction and photooxidation of water. This is in line with the demonstrations of hydrogen[10,13) and oxygen[37) evolutions at illuminated Chl electrodes with use of acidic and alkaline electrolyte solutions, respectively.

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