# PHOTOELECTROCHEMICAL STUDIES ON THE MONOLAYER ASSEMBLIES OF CHLOROPHYLL *a* ON THE QUANTUM EFFICIENCY OF PHOTOCURRENT GENERATION

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Characteristics and quantum efficiencies of photocurrents at monolayer, mixed monolayers, and multilayers of chlorophyll *a* deposited on semiconducting $SnO_2$ electrodes and/or metal electrodes were surveyed. The quantum efficiency of photocurrent depends on the surface concentration of chlorophyll *a* as well as the thickness of layers. The photocurrent behavior of chlorophyll *a* multilayers is compared between $SnO_2$ surface and metal electrode surface. The highest efficiency is obtained with a homogeneously mixed monolayer of chlorophyll *a*-lecithin on $SnO_2$. The usefulness of such monolayer assemblies in the photoelectrochemical studies of chlorophylls is emphasized.

## 1. Introduction

The use of biological pigments or their model compounds as photoreceptors for visible light conversion has established itself as one of the major fields in current photoelectrochemistry. Chlorophyll (Chl) *a*, which is involved in water-splitting reaction centers in photosynthesis, has been of special interest not only for its high redox reactivity but also for its advantage in utilizing the red region of solar energy. During the last few years, there have been reported various modes of photoelectrochemical cells using in vitro Chl *a* molecules [1–6]. In such systems, one of the important aspects which are evaluated is the quantum yield of light conversion.

From surface chemical aspects, Chl *a* molecule, which consists of a porphyrin ring with hydrophilic carbonyls and a hydrophobic phytol, acts as an ideal membrane-forming pigment in and on an aqueous phase. This property has been employed in the study of bilayer lipid membrane (BLM) [6, 7]. Monolayer and mixed monolayers of Chl *a* have also been well investigated using the Langmuir technique [8–11]. The usefulness of such monolayer assemblies for the photoelectrochemical investigation is emphasized in the following advantages: (1) the facility of coating dye on an

electrode, (2) the formation of a homogeneous dye layer which permits the control of surface concentration of the dye, and (3) the precise regulation of the total thickness of dye layers.

Recently, we have studied the photoelectrochemical behavior as well as the quantum conversion efficiencies of a series of monolayer assemblies of Chl $a$ on $SnO_2$ electrodes [12–14]. Based on these investigations, this paper will compare the quantum efficiencies of photocurrents obtained with different arrangements of Chl $a$ monolayers on $SnO_2$, focussing the discussion on the energy transfer and dissipation within Chl $a$ layers. We also provide a discussion of the distinction in photoelectrochemical behavior between semiconductor–Chl $a$ interface and metal–Chl $a$ interface.

## 2. The monolayer technique for photoelectrochemical investigations

Fresh Chl $a$, which is usually extracted from spinach by a general procedure (see ref. [12]), is required for the preparation of the monolayer. A monolayer of pure Chl $a$ and a mixed monolayer of Chl $a$ – diluent (such as a fatty acid or a phospholipid) are formed on an aqueous subphase (phosphate buffer, pH 8) in a Langmuir trough. Benzene or diethylether is used as a spreading solvent [8–11]. The physical properties of a monolayer formed on an aqueous surface, such as collapse pressure, surface density, surface dipole moment, and homogeneity in a two-dimensional structure, can be examined through the measurements of the surface pressure-area (F–A) isotherm and surface potential [8, 10, 13]. In general, the Chl $a$ monolayer tends to collapse at a surface pressure of 23–25 dyn/cm, which corresponds to the molecular area of 80–90 Å$^2$ [8, 12]. The optical properties for a Chl $a$ monolayer have been reported by several workers and are summarized in ref. [12]; the red absorption peak of the monolayer at 20 dyn/cm is situated at 676–679 nm with an absorbance of 0.008–0.009 per layer.

For the photoelectrochemical measurement, the monolayer thus formed on the aqueous surface is transferred onto the surface of a substrate (electrode), by slowly moving upward the electrode across the water surface under a constant surface pressure (20 dyn/cm generally employed in our studies) [12]. The multilayers of Chl $a$ and a Chl $a$ – diluent mixture can be built up on solid substrates [10, 14]. As the electrode for the monolayer deposition, we have employed optically transparent electrode (OTE) of semi-conducting $SnO_2$ (thickness of $SnO_2$ layer, ca. 2000 Å; donor density, $4 \times 10^{20}$/cm$^3$) [12–14]. For comparison, a metal electrode (Pt plate, 0.05 mm thick) was also examined.

The electrochemical setup for the photocurrent measurement consists of a light source (500 W xenon arc lamp), monochromator, picoammeter,

potentiostat, and an electrochemical cell. The detailed description for this setup including the construction of the cell is represented in the previous paper [12].

## 3. Generation and quantum efficiency of photocurrent at $SnO_2$–Chl $a$ interface

The photocurrent generation at the $SnO_2$–Chl $a$ interface obeys the general mechanism of dye sensitization on an n-type semiconductor, which has been postulated by many researchers using a variety of dye–semiconductor combinations [15, 16]. $SnO_2$ [17] is a typical semiconductor which is intrinsically not photoexcited in the visible region because of its large forbidden gap of 3.5–3.8 eV (corresponding to 354–326 nm), and for this advantage $SnO_2$ OTE has been generally utilized for studies of dye-sensitized (or -modified) electrodes [18–21].

Fig. 1 illustrates schematically the processes of electron transfer and possible energy dissipation at $SnO_2$–Chl $a$ and Chl $a$–electrolyte interfaces. The electron injection from an excited Chl $a$ into the conduction band of $SnO_2$ ($a$), which causes anodic photocurrent, can take place with a high efficiency, since the oxidation potentials of both the excited singlet ($S^*$) and triplet ($T^*$) states, $-1.31$ and $-0.79$ V versus saturated calomel electrode (SCE), respectively [22], are sufficiently higher than the conduction band edge of $SnO_2$ (close to the flatband potential, $-0.35$ V versus SCE at pH 7 [17]). Other possible electron transfer processes, such as ($b$) electron ejection from the excited Chl $a$ to reducible species in electrolyte, e.g., oxygen, ($c$) tunnelling of conduction band electrons through thin space charge layer toward the half-vacant level of grand state Chl $a$, and the energy dissipation of excited Chl $a$ via ($d$) energy transfer to the conduction band mobile electrons or ($e$) internal conversion to the ground state, can
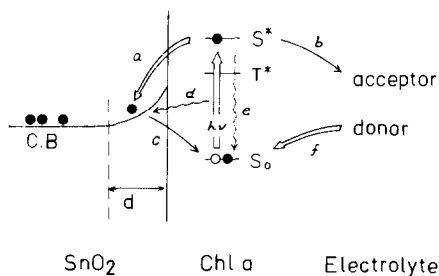


Fig. 1. Schematic illustration for electron and/or energy transfers at semiconductor ($SnO_2$)–Chl $a$ and Chl $a$–electrolyte interfaces. CB, conduction band; d, space charge layer thickness. For the correlation of each path, ($a$)–($f$), see text.

equally lower the overall efficiency of anodic photocurrent. The process (*b*) can be minimized by purging the oxidants such as dissolved $O_2$ in electrolyte. Under sufficient anodic polarization of the electrode, the other processes, (*c*)–(*e*), could become almost negligible when the semiconductor possesses a lower doner density giving a thicker space charge layer (see fig. 1), and an electrolyte contains an adequate supersensitizer (electron doner) which can rapidly reduce the oxidized dye (process (*f*)). For example, a quantum efficiency close to unity has been reported for the dye-sensitized photocurrent on ZnO [15]. In case of $SnO_2$ OTE, which has a high donor density (i.e., a thin space charge layer), the processes (*c*) and/or (*d*) may compete with normal processes, (*a*) and (*f*), and hence could control the maximum quantum efficiency of the photocurrent, particularly under less anodic polarization of the electrode giving the thinner space charge layer (see ref. [12]). In order to compare the photocurrent efficiencies of different Chl *a* films on $SnO_2$, the present paper deals with the maximum quantum efficiencies obtained in each system by selecting the optimum condition of anodic polarization.

The quantum efficiency of photocurrent generation defined as electrons flowing per photon absorbed by the dye layer can be calculated by the following equation:

$$\phi_\lambda = (I_{p\lambda}/q)/F_\lambda(1 - 10^{-A_\lambda})(1 + f_\lambda \times 10^{-A_\lambda}) \ .$$

where $\phi_\lambda$, $I_{p\lambda}$, $F_\lambda$, and $A_\lambda$ represent the quantum efficiency, the observed photocurrent (A/cm²), the incident photon flux (photons/cm² · s), and the absorbance of the dye layer at electrode–electrolyte interface, respectively, at wavelength $\lambda$ (nm). The constant $q$ is the electron fundamental charge (C). Here, $f_\lambda$ serves as a correction factor of incident flux for its reflectance at the electrode surface. The factor $f_\lambda$ is almost negligible for $SnO_2$ OTE but should be taken into account in case of normal metal plate electrodes. Using $SnO_2$ OTE, the calculation of quantum efficiency becomes easy and precise since the good transmittance of the OTE (80–90% versus air in the visible region) permits a direct measurement of in situ absorption of the dye layer in contact with an electrolyte solution.

## 4. Chl *a* monolayer and mixed monolayers on $SnO_2$

A typical action spectrum of anodic photocurrent for a pure Chl *a* monolayer, which was measured in the presence of 0.05M hydroquinone ($H_2Q$) in an electrolyte as a reducing agent, is demonstrated in fig. 2 where the magnitudes of the photocurrents are normalized for constant incident flux. The observed photocurrent spectra at such Chl *a* monolayer assemblies were essentially identical with their absorption spectra at the $SnO_2$–electrolyte interface. Dependence of the Chl *a* photocurrent on electrode
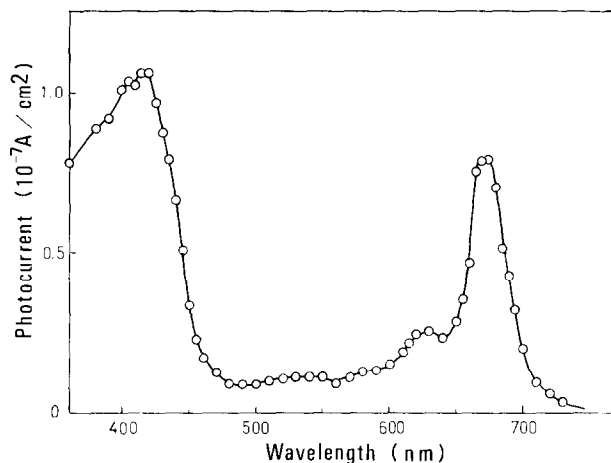
Fig. 2. Photocurrent action spectrum of Chl *a* monolayer on $SnO_2$ electrode [12]. Surface pressure for monolayer deposition, 20 dyn/cm; electrolyte composition, $H_2Q$ 0.05M, $Na_2SO_4$ 0.05M, and phosphate buffer 0.025M (pH 6.9); electrode potential, 0.05 V versus SCE.

potential, concentration of $H_2Q$, pH of electrolyte, and other detailed characteristics of the photocurrent are summarized in an earlier paper [12].

A mixed monolayer consisting of Chl *a* and an inert diluent, such as a fatty acid or a phospholipid, is of special importance for the study of the intermolecular energy transfer. For instance, enhancement of fluorescence yields for mixed monolayer systems upon decreasing the surface concentration of Chl *a* (i.e., increasing the intermolecular distance between Chl *a*) has been investigated by Tweet et al. [9] and Porter et al. [12], and the enhancement is attributable to a decrease of intermolecular quenching of excitation energy, i.e., self-quenching, upon the two-dimensional dilution of Chl *a*. In the photoelectrochemical processes, the energy transfer between dyes adsorbed on the electrode surface, which is enhanced at high dye concentrations, results in the lowering of photocurrent efficiency, because such an energy transfer leads eventually to the energy dissipation in terms of, e.g., self-quenching among dye molecules.

Based on this concept, using mixed monolayers in various molar ratios, we have previously studied the dependence of photocurrent quantum efficiency on the surface concentration of Chl *a* [12, 13]. As two-dimensional diluents for Chl *a*, stearic acid ($C_{18}$) and dipalmitoyllecithin (DPL) were examined. The electrolyte consisting of 0.1M $Na_2SO_4$, 0.05M $H_2Q$, and 0.025M neutral phosphate buffer, and an electrode potential of 0.1 V versus SCE were employed throughout the experiments. The results are given in fig. 3 for these two diluent systems. In the Chl *a* – DPL mixed monolayer system, the quantum efficiency tends to increase with lowering the surface
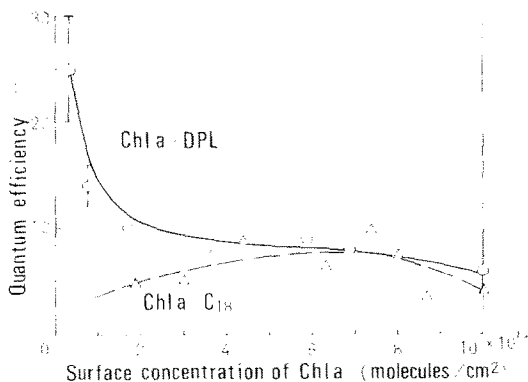
Fig. 3. Dependence of photocurrent quantum efficiencies of Chl $a$–stearic acid ($C_{18}$) and Chl $a$–dipalmitoyllecithin (DPL) mixed monolayers on the surface concentration of Chl $a$. Quantum efficiencies were measured at blue bands of photocurrent spectra. Surface pressure of deposition, 20 dyn/cm; electrolyte, $H_2Q$ 0.05M, $Na_2SO_4$ 0.1M and phosphate buffer 0.025M (pH 6.9); electrode potential, 0.1 V versus SCE.

concentration of Chl $a$ until it reaches a maximum of $25 \pm 5\%$ [13]. On the other hand, the Chl $a$–stearic acid system does not show a good enhancement effect with such a dilution [12]. The observed distinction between the two systems would reflect the difference in the surface homogeneities of mixed monolayers. The examination of the F–A isotherms of both mixed monolayers revealed that DPL behaves as an ideal two-dimensional diluent for Chl $a$ to form a homogeneous monolayer [13], while stearic acid may form a partially heterogeneous mixed layer with Chl $a$. Thus, we conclude that the homogeneously and highly diluted Chl $a$ monolayer can give a higher efficiency of electron injection into $SnO_2$ (i.e., photocurrent generation) due to a suppressed energy transfer between Chl $a$, and the heterogeneity of Chl $a$ molecules causing an intermolecular energy quenching must be responsible for the lower photocurrent efficiency in the Chl $a$–stearic acid system.

Maximum quantum efficiency obtained with the Chl $a$–DPL system is of considerable value and is supposedly close to the upper limit of the efficiency obtained for dye-sensitized $SnO_2$ OTE [19–21] in view of the possible energy-dissipating processes as discussed in the preceding section.

## 5. Chl $a$ multilayers on $SnO_2$

When a relatively thick layer of Chl $a$, e.g., amorphous film and micro-crystalline layer, is coated on a metal electrode, a cathodic photocurrent can generally be observed [2–5, 24, 25], due possibly to the p-type photo-

conductivity of a Chl *a*–metal contact. To investigate the photocurrent behavior of thick layers of Chl *a*, we attempted to build up various numbers of Chl *a* monolayers on $SnO_2$ OTE. It was found that Chl *a* multilayers on $SnO_2$ always give anodic photocurrents either in the presence or in the absence of $H_2Q$, owing to a rectifying property of the semiconductor. In the case where the electrolyte contained a trace of dissolved oxygen, a cathodic photocurrent due to the reduction of $O_2$ by excited Chl *a* was detected under cathodic polarization of the electrode. Such an effect of dissolved oxygen and other detailed behavior of photocurrent are described elsewhere [14].

The quantum efficiency of the anodic photocurrent in an electrolyte containing 0.05M $H_2Q$ was measured for a series of different numbers of monolayers. The results showed that while the magnitude of the photocurrent could be enhanced by increased number of layers, the quantum efficiency simply decreased with increasing the number of layers (i.e., the thickness of film). Such a suppression of photocurrent efficiency would arise from an increase in inner electric resistance of multilayer and an enhancement of intermolecular energy transfer, i.e., energy dissipation, between Chl *a* molecules in three-dimensionally packed layers. The same phenomenon can be expected generally for the spectral sensitizations at the dye layer-deposited n-type semiconductors. Consequently, the above investigations confirm that a single mixed monolayer is most efficient for light conversion using the Chl *a*–n-type semiconductor combination.

## 6. Chl *a* films on metal electrodes

Metal electrodes (mainly Pt) have commonly been employed as substrates of Chl *a* films in electrochemical photocells [2–5]. In such systems, the Chl *a*–metal electrode behaves as a photocathode in the presence of suitable acceptor species. Based on the general assumption in photoelectrochemistry, however, such a photocurrent obtained with a metal electrode should be much less efficient than that gained with a semiconductor electrode, owing to (i) the efficient energy quenching of the excited dye by free electrons in the metal (as a main cause) and (ii) the reversibility of electron transfer between metal surface and dye (for further discussion, see refs. [16, 26]). Occurrence of (i) has been verified by Kuhn and co-workers, using dye monolayers on metals [27].

Based on this concept, we investigated the photocurrent behavior as well as quantum efficiencies at Chl *a* multilayer-coated Pt electrodes. Experimentally, multilayers consisting of Chl *a* and DPL (molar ratio 1/1) were built up on Pt plates and their photocurrents were measured under potentiostatic conditions in an electrolyte of 0.1M $Na_2SO_4$ which was flushed

with $N_2$. When relatively thick multilayers were illuminated, cathodic photocurrents of measurable values were generated under the cathodic polarization of the electrode, while no significant photocurrent was obtained for a single mixed monolayer on Pt. The photocurrent–potential curve measured for a stack of 21 mixed monolayers is given in fig. 4. The onset potential for the cathodic photocurrent is around +0.4 V versus SCE, which is somewhat higher than the oxidation redox potential of Chl $a$ (+0.54 V [22]). The magnitude of the photocurrent was enhanced by decreasing the pH of the electrolyte solution, indicating that some redox species in the electrolyte could act as an electron acceptor for excited Chl $a$. From these results, we assume that the reaction would proceed by the photooxidation of Chl $a$ and subsequent electron transfer from metal surface to the oxidized Chl $a$.

The maximum quantum efficiency in this system, estimated with taking into account the surface reflectance of Pt, was in the order of $10^{-4}$, even when the electrolyte contained oxygen (as an acceptor). This value is not comparable with those obtained with Chl $a$ on $SnO_2$ ($10^{-2}$–$10^{-1}$), as was predicted theoretically. However, in the system which involves special species of Chl $a$, e.g., microcrystalline Chl $a$ having a p-type organic photoconductivity [2, 24, 25], the other aspect of the quantum efficiency as well as the mechanism of photocurrent generation than investigated here could be expected.

## 7. Concluding remarks

In an electrolyte without added redox agents, Chl $a$ monolayers on $SnO_2$ give anodic photocurrents while those on metal electrodes exhibit cathodic photocurrents. In the present study, the highest efficiency of photocurrent was obtained with a sufficiently diluted homogeneous monolayer of Chl
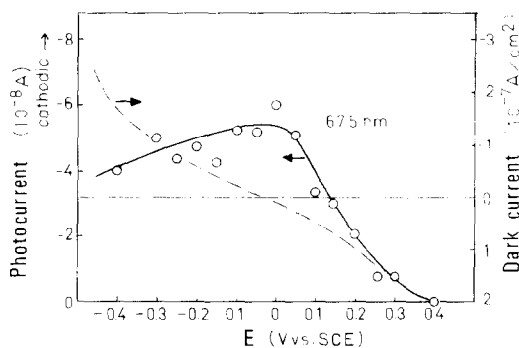


Fig. 4. Photocurrent–potential characteristics of Chl $a$–DPL multilayer (21 layers) on Pt electrode Dashed line represents a background dark current. Electrolyte, 0.1M $Na_2SO_4$ (pH 7).

$a$–DPL on $SnO_2$. Upon the two-dimensional dilution of Chl $a$, however, the magnitude of photocurrent is lowered owing to the decrease of absorbance. Consequently, the alignment of a number of mixed monolayer-coated $SnO_2$ electrodes in parallel makes it possible to design a light conversion system with high quantum efficiency as well as high yield of light absorption.

## Acknowledgements

The authors thank Dr. A. Fujishima and Dr. T. Watanabe for their helpful discussion. The authors are grateful to Professor R.M. Leblanc at University of Québec at Trois-Rivières for his interest.

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