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Photoelectric Conversion with the Dye Multilayer on a Semiconductor Electrode

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Photoelectric conversion with the dye-containing multilayers on an Sb-doped SnO_2 optically transparent semiconductor electrode was studied, using 2,8-bis(dimethylamino)-10-dodecyl-acridinium bromide (BDA) and dioctadecylthiacarbocyanine iodide (DTC). A remarkable enhancement of the photocurrent was observed as a result of the efficient energy transfer from BDA to DTC.

The use of dye-containing monolayers and multilayers formed by the Langmuir-Blodgett technique[1] has a very attracting feature.[2-5] Photoelectric conversion using the dye-containing monolayer on a semiconductor electrode has been reported.[6,7] Arden and Fromherz[8] and Fujihira et al.[9] have studied the photoelectric conversion by the dye-containing multilayer on the semiconductor or gold-OTE electrode, in which two dyes, the sensitizing dye and the electron-injecting dye, were incorporated in the adjacent monolayers. Sensitization of silver halide evaporated layers using the multilayer assembly in which the electron-injecting dye is in contact with the halide layers and the sensitizing (energy donor) dye is at the distance of 54 Å was shown by Steiger et al.[10] In the present paper, we studied the sensitized photocurrent of the dye-containing multilayers on a semiconductor electrode, with particular emphasis on the role of the sensitizing dye separated from the electron-injecting dye by more than two fatty-acid monolayers.

The multilayer of arachidic acid was deposited by the Langmuir-Blodgett technique[1] on the optically transparent Sb-doped SnO_2 substrate (Tokyo Eriko) which was used as a semiconductor electrode. Two kinds of dyes were incorporated in multilayers: 2,8-bis(dimethylamino)-10-dodecyl-acridinium bromide (hereafter denoted as BDA) was deposited in the "outer" layer which was separated from the semiconductor with arachidic acid monolayer(s), dioctadecylthiacarbocyanine iodide (DTC) was incorporated in the "first" layer in direct contact with the semiconductor. BDA and DTC purchased from Dojin and Japanese Research Institute for Photosensitizing Dyes, respectively, were used as received. BDA excited by external illumination transfers the excitation energy to DTC. Then, DTC transfers an electron to the semiconductor electrode. Various types of monolayers and multilayers were prepared. In blank experiments with BDA only, the monolayer and multilayers shown in Fig. 1, (a)-(d) were used. The arachidic acid monolayer(s) was used for the spacer in some cases. In the experiments with BDA and DTC, the monolayer and multilayers (e)-(h) were used. The molar ratio of dye to arachidic

acid in each monolayer was always 1 : 10, except for the monolayer containing both of BDA and DTC (i.e. (e) in Fig. 1), where the ratio BDA:DTC:arachidic acid was 1:1:6.

In the photocurrent measurements, the potential of the SnO_2 electrode was controlled by a potentiostat at +1.0 V vs. SCE. The counter electrode was a platinum plate. Water was doubly distilled. The supporting electrolyte was KCl (0.5 M). (1 M = 1 mol dm^{-3}) Thiourea (1 M) was added as a supersensitizer.[11] A 150W xenon arc lamp in combination with a Hitachi model 650-10S spectrofluorometer was used as a light source in the measurement of action spectra of the photocurrent. The measurement of the intrinsic current quantum efficiency was made with the 476.5nm line from a Spectra-Physics Model 165 Ar^+ laser. The exciting light was chopped at 15 Hz. Photocurrent was measured with an NF Electronic Instruments Model LI-570 lock-in amplifier with a Model LI-75A preamplifier. The same measurement was repeated with 5 - 10 samples. All measurements were made at room temperature for aerated solutions.

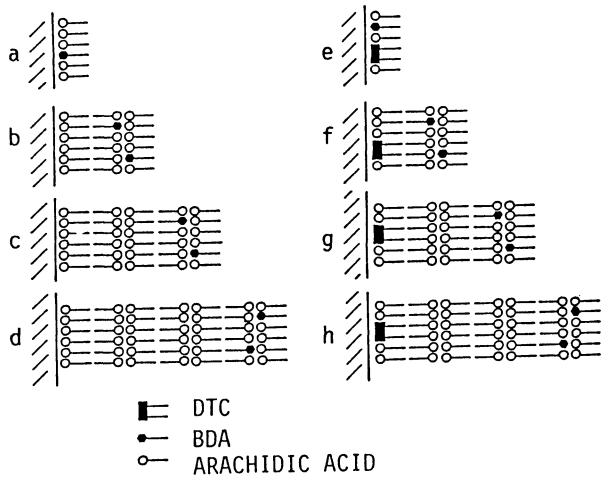

Fig. 1. The structure of multilayers. Multilayers (a)-(d) were used for experiments with only one dye (BDA) and (e)-(g) for experiments with two dyes (BDA and DTC). DTC was deposited on the substrate directly.

Firstly, the results of experiments with two dyes (BDA and DTC) are described. An efficient energy transfer can be expected between these two dyes, in view of the high fluorescence yield of the energy donor (BDA) and the good spectral overlap of its fluorescence band with the absorption band of the energy acceptor (DTC).

The curve (i) in Fig. 2 shows a typical absorption spectrum of the multilayer containing DTC and BDA ((g) in Fig. 1). The curve (ii) shows that of the monolayer containing DTC. The ratio of DTC to arachidic acid was 1 : 10. Clearly, the absorption of exciting light by DTC is very small compared to that of BDA. Absorption maximum in the curve (i) at 470nm is due to the dimer of BDA. The monomer band appeard as a shoulder at 490 nm. A large portion of BDA molecules is dimerized in the layer.

Fig. 3 shows a typical photocurrent action spectrum of the multilayer (g). This spectrum is very much alike the absorption spectra of Fig. 2(i). We can conclude that the photocurrent was caused mainly by the excited BDA. The contribution of direct excitation of DTC to the photocurrent is very small.

The efficiency of electron injection was determined in terms of the intrinsic current quantum efficiency (η), which is defined for a single excitation wavelength as

$$\eta = n_e/n_{ph}, \qquad (1)$$

where n_e is the number of electrons which flow through a circuit and n_{ph} is the number of photons absorbed by the dye. The n_e was estimated from the photo-

current at 476.5 nm, and n_{ph} was estimated from the absorbance of BDA in the multilayer at the same wavelength. The curve (ii) in Fig. 4 shows the dependence of η on the distance between the BDA and semiconductor in the presence of DTC.

Secondly, the results of blank experiments with one dye (BDA) are discussed. The photocurrent action spectrum for the monolayer (a) was very much alike its absorption spectrum. For multilayers (b) and (c), we observed a small photocurrent (ca. 7% and 0.04% of (a), respectively). No observable photocurrent was obtained for the multilayer (d). The η values for these monolayer and multilayers are shown by the curve (i) of Fig. 4. Arden and Fromherz[8] observed the electron transfer across two tenside layers on the SnO_2 semiconductor electrode with the transfer efficiency of 8-9%. They attributed it to the imperfection of the layers. The photocurrent observed for the multilayers (b) and (c) is probably due to the imperfection of the layers.

Comparison of the curves (i) and (ii) in Fig. 4 clarifies the effect of the addition of DTC. The addition of DTC remarkably increases η for the multilayers (g) and (h) compared to the corresponding blank, (c) and (d). Since the photocurrent in (c) and (d) was more than one order of magnitude smaller than that in (g) and (h), respectively, the observed photocurrent for (g) and (h) is essentially the sensitized one that is caused by the energy transfer from excited BDA to DTC, followed by the electron transfer from DTC to the semiconductor. A remarkable enhancement of the photocurrent as compared to the cases without DTC is due to the efficient energy transfer from BDA to DTC. Here, BDA works like the antenna chlorophyll and DTC like the reaction-center chlorophyll in the chloroplast.

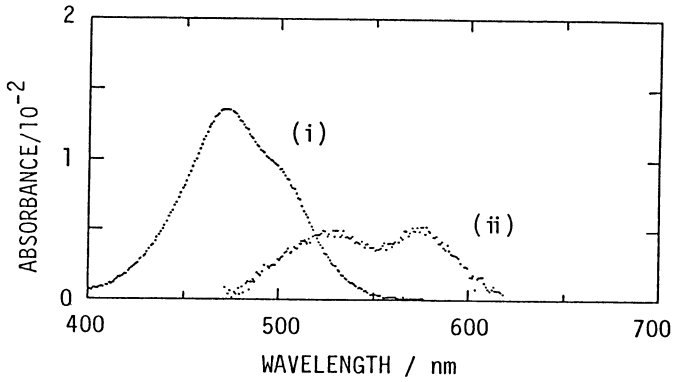

Fig. 2. Absorption spectra. (i): multilayer (g) containing BDA and DTC, (ii): monolayer of DTC in arachidic acid (1 : 10). For (ii), absorbance is multiplied by a factor of 5.

However, the addition of DTC reduced η when DTC was incorporated in the first monolayer with BDA (monolayer (e) in Fig. 1). Apparently DTC acts as a quencher here. In this case η is given as

$$\eta = \eta_{BDA}(1 - \phi_{ET}) + \phi_{ET}\eta_{DTC} \quad (2)$$

where ϕ_{ET} is the quantum efficiency for the energy transfer in the same monolayer. η_{BDA} and η_{DTC} are, respectively, η of BDA and DTC in direct contact with the electrode. Clearly, the result shows η_{DTC} <

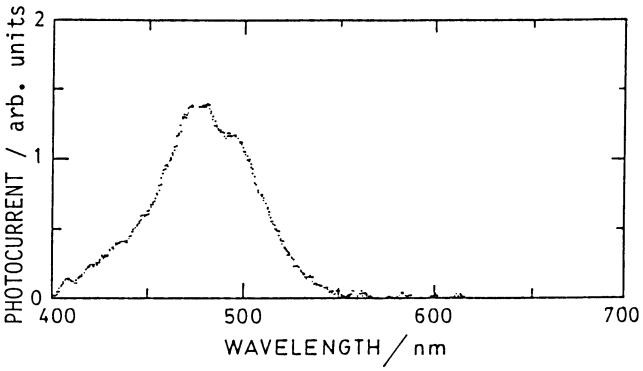

Fig. 3. Photocurrent action spectrum of the multilayer (g) containing BDA and DTC, normalized to the incident photons.

η_{BDA}. An improvement in η can be expected when a dye with $\eta \geq \eta_{BDA}$ is used instead of DTC.

In conclusion, a remarkable enhancement as compared to the cases in which only BDA was used was found in the photocurrent with the multilayer system when BDA was incorporated in the outer layer, by the presence of DTC in the first layer in direct contact with the semiconductor electrode.

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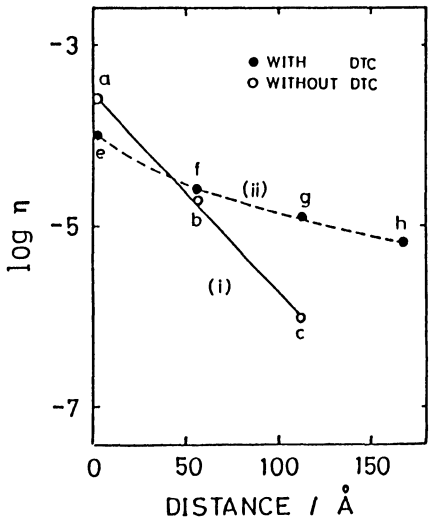

Fig. 4. Logarithm of the intrinsic current quantum efficiency (η) versus distance between BDA and semiconductor. Solid line: BDA only, Broken line: BDA plus DTC. The multilayer (d) gave no measurable photocurrent.

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11) The supersensitizing mechanism of thiourea for the multilayers (f), (g), and (h) is not clear at present. Some of thiourea molecules may be present in the vicinity of DTC due to the imperfection of the layers and/or diffusion through the layers.

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