CHEMISTRY LETTERS, pp. 1399-1402, 1980.

ENHANCEMENT OF PHOTOCURRENT AT A MEROCYANINE-COATED ELECTRODE DUE TO CHROMOPHORE AGGREGATION

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Remarkable absorption spectral change and enhancement of photocurrent due to chromophore aggregation have been achieved by treating a cast film of a new surface-active and photo-active merocyanine dye on an optically transparent SnO_2 electrode with an alkaline aqueous solution.

Recently, the merocyanine solar cells with high sunlight efficiency have been developed.[1-3] Subsequently, we have developed a new surface-active and photo-active merocyanine dye (MD) shown in Fig.1.[4,5] The mixed monolayers of the MD with arachidic acid have shown a weak red-shifted absorption due to a J-like aggregation.[5] A red-shifted band such as a J-band[6] has been expected to give an enhanced photoelectric effect,[7] whereas a blue-shifted aggregate has been reported to be less photo-active than the monomer.[8] It has been found that the visible absorption spectrum of a cast film of the MD on an optically transparent SnO_2 electrode (OTE) is drastically changed to form the J-like band by soaking the film in an alkaline aqueous solution, and that the photocurrent of the pigmented electrode thus treated is enhanced. In this article, we report the preliminary results.

1.5 cm^3 of 0.33 mmol dm^{-3} solution of the MD in $CHCl_3$ was placed drop by drop on the OTE (Matsuzaki Shinku; 3.3 X 5.0 cm^2 in size) and then dried to produce a homogeneous cast film which contained 3 X 10^{-8} mol cm^{-2} of the MD.

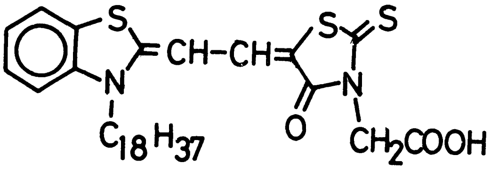

Fig. 1. Chemical structure of the merocyanine dye (MD).

Absorption spectra of the MD solution and the pigmented electrodes were recorded by using Shimadzu double-beam spectrophotometer UV-220. Photoelectrochemical measurements were carried out by employing the procedures described in earlier papers.[4,9] The pigmented electrode was mounted as a window of the electrochemical cell to give an available area of 4.0 cm^2. An aqueous solution of 0.5 mol dm^{-3} HCl (pH 0.4) was used as the electrolyte. Oxygen was expelled from the electrolyte by bubbling argon through it, and the temperature was kept at 25 ± 1 °C. A 500-W xenon ark lamp with interference filters (400-660 nm; band width *ca.* 10 nm) was

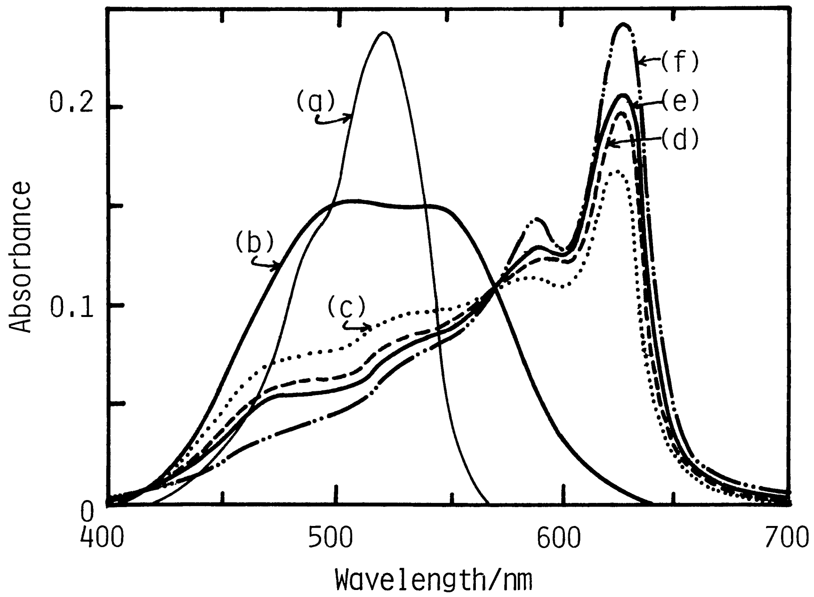

Fig. 2. Absorption spectra of (a) 0.14 mmol dm^{-3} MD in $CHCl_3$ and (b) the cast film of the MD on OTE and absorption spectral change of the MD film on OTE in 0.1 mol dm^{-3} NaOH solution at 25 °C as a function of time. Curves (c), (d), (e) and (f) are the absorption spectra of the MD film after soaking in the NaOH solution for 5 min, 15 min, 30 min, and 240 min, respectively.

employed as the light source on the pigmented electrode from the OTE side. 5 cm of a water layer and a ND filter (transmittance 0.1) were placed between the lamp and the interference filter.

Fig. 2 shows the visible absorption spectra of (a) the MD solution in $CHCl_3$ and (b) the cast film of the MD on the OTE. The peaks at 516 nm and 546 nm on the spectrum (b) can be assigned to the dimeric (or oligomeric) and monomeric forms of the MD molecules in the films, respectively, because the absorption at 516 nm decreases when the MD in the film is diluted by addition of arachidic acid.

The absorption spectrum of the MD film is changed by soaking it in an alkaline aqueous solution of 0.1 mol dm^{-3} NaOH (see curves (c), (d), (e) and (f) in Fig. 2). Two isosbestic points are observed around 410 nm and 570 nm. After the alkaline treatment for 240 min, the

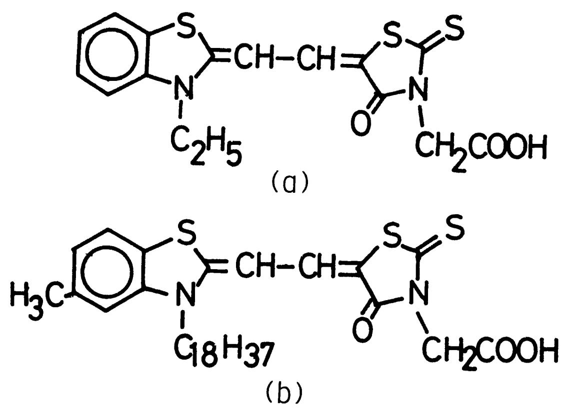

Fig. 3. Chemical structure of (a) the MD-2 and (b) the MD-3.

film was dissolved in $CHCl_3$ and then the solution was examined by thin-layer chromatography.[3)] It was confirmed that the spectral change is not due to the degradation products in the course of soaking.

It has been found that the film of the merocyanine dye (MD-2), in which $-C_{18}H_{37}$ of the MD is replaced by $-C_2H_5$ (see Fig. 3 (a)), did not show any red-shifted absorption peak by soaking it in the NaOH solution. In addition, the film of the other merocyanine dye (MD-3) with $-CH_3$ at 5-position in the benzthiazoline group (see Fig. 3 (b)) showed no red-shifted band by the alkaline treatment.[11)] These results suggested that the spectral change of the MD film is interpreted in terms of some sort of chromophore aggregation rather than the simple reaction of each molecule such as the dissociation of carboxyl group or some isomerization. The absorption peak around 620 nm is sharp as seen in Fig. 2. We cannot miss the apparent similarity between the present red-shifted band and those of J-aggregates formed in the Langmuir multilayers.[6)] However, a narrow and strong resonance emission peak which is characteristic for the J-aggregates[12)] has not been observed, and only a weak emission was observed around 630-640 nm. Detailed analyses of the 620-nm absorption band is currently under investigation.

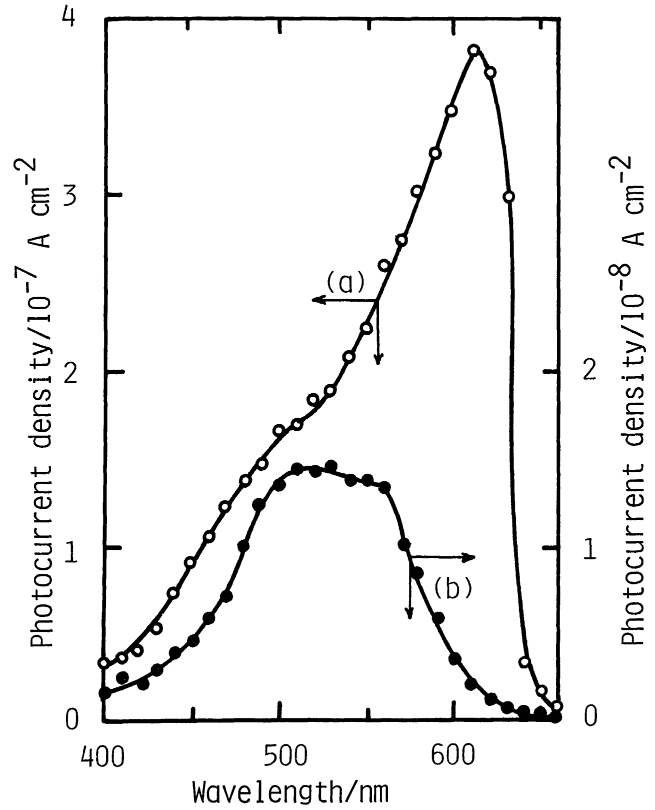

Fig. 4. Photocurrent spectra at the pigmented electrodes (a) with and (b) without the alkaline treatment for 30 min. The spectra were taken in 0.5 mol dm^{-3} HCl solution at 0.3 V *vs.* SCE at 25 °C, and are normalized for an incident level of 1×10^{15} photons cm^{-2} s^{-1}.

The measurements of photocurrents were carried out by using two types of the pigmented electrode, with or without the treatment in the NaOH solution for 30 min. The absorption spectrum of each electrode remained almost unchanged in 0.5 mol dm^{-3} HCl solution for at least 120 min. Figs. 4 (a) and (b) show the photocurrent spectra of the pigmented electrodes with and without the alkaline treatment, respectively, under the potentiostatic condition (0.3 V *vs.* SCE). Cathodic photocurrent for hydrogen generation[10)] are observed at both electrodes at the potential which is *ca.* 0.6 V more positive than the thermodynamic potential. The photocurrent is remarkably enhanced by the treatment even in the wavelength region of 410-570 nm, in which the absorbance is decreased. The quantum efficiency at 500 nm was increased from 3×10^{-4} to 9×10^{-3} by the treatment.

The photocurrent spectra of both

types of the pigmented electrode were not virtually influenced by the surface density of the MD in 1-6 X 10^{-8} mol cm^{-2}.

The photocurrent spectrum of the electrode without the alkaline treatment is reasonably coincided with the absorption spectrum of the electrode (see Figs. 4 (b) and 2 (b)). However, the photocurrent spectrum of the electrode with the alkaline treatment is rather different from the absorption spectrum (see Figs. 4 (a) and 2 (e)). So far, the difference between the photocurrent and the absorption spectra as well as the mechanism of the increment of photocurrent due to the chromophore aggregation cannot be decisively interpreted. Further investigation shall be given to clarify the mechanism.

In summary, we have found the chromophore aggregation associated with the enhanced photocurrent at the pigmented electrode by the simple treatment.

The authors are grateful to Dr. Michio SUGI for his informative suggestions and helpful discussions. The authors appreciate Dr. Shigeo YASUI for providing the merocyanine dyes used in the experiments.

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(Received July 4, 1980)