

## ATTEMPT FOR THE CONSTRUCTION OF PIGMENTED ELECTRODE

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A flexible pigmented electrode has been developed by depositing a merocyanine film on a transparent electro-conducting film and its electrochemical behavior has been studied.

Recently, Moriizumi and Kudo<sup>1)</sup> have developed a merocyanine-dye photovoltaic cell on a plastic film by aiming to construct a light, flexible, and large-area solar cell. On the other hand, we have achieved the electrochemical photolysis of water at an  $\text{In}_2\text{O}_3$  electrode coated with merocyanine dye<sup>2)</sup> as well as the enhancement of photocurrent at a merocyanine-coated electrode due to chromophore aggregation.<sup>3)</sup> In this article, we report a flexible pigmented electrode and its electrochemical behavior.

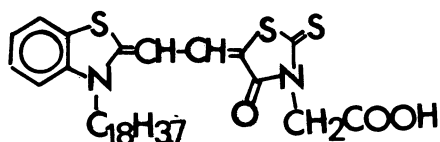


Fig. 1. Chemical structure of the merocyanine dye.

The merocyanine dye (MD) used in the present experiments, whose chemical structure is shown in Fig. 1, was synthesized according to the procedures of Brooker *et al.*<sup>4)</sup> with the additional modifications.<sup>5)</sup> The transparent electro-conducting film was a polyester film coated with ITO (indium-tin oxide), whose transparency and sheet resistivity were 86 % for the average solar spectrum region and  $500 \Omega/\square$ , respectively. The flexible electrode was produced by Teijin, Ltd., Japan.

A homogeneous liquid-cast film of the MD on the electro-conducting plastic film was prepared according to the exactly same procedures previously described.<sup>3)</sup> It was found that the plastic film was chemically stable under the present experimental conditions unless otherwise stated. Absorption spectra of the pigmented electrodes were recorded on a Jasco UVIDEK-1 double-beam spectrophotometer. Electrochemical measurements were conducted by employing the same procedures under the completely same experimental conditions previously described.<sup>3)</sup>

In the previous report,<sup>3)</sup> we have found the remarkable absorption change and enhancement of photocurrent due to chromophore aggregation by treating a merocyanine-coated  $\text{SnO}_2$  electrode in alkaline solution. Subsequently, we have studied absorption changes of the pigmented electrodes by treating them in various kinds of neutral or alkaline solutions.<sup>6)</sup> Fig. 2 illustrates the absorption spectra of the pigmented plastic electrode before and after the treatment in  $10^{-4}\text{M}$  phosphate buffer (pH 7.0). Immersion of the dye-coated electrode in the buffer solution induced gradual decrease of the absorption intensities at 516 nm and 546 nm in accordance with the increase of the absorption intensity at 600 nm showing two isosbestic points around 410 nm and 568 nm.

Figs. 3 (a) and (b) show the photocurrent spectra of the pigmented electrodes without and with the buffer treatment, respectively, under the potentiostatic condition (0.3 V *vs.* SCE). The photocurrent is remarkably enhanced by the simple treatment. The quantum efficiencies for photocurrent generation at the electrodes without and with the treatment were found to be 0.042 % at 546 nm and 0.43 % at 600 nm, respectively.

As described above, the photoelectrochemical cell with the pigmented flexible electrode with the

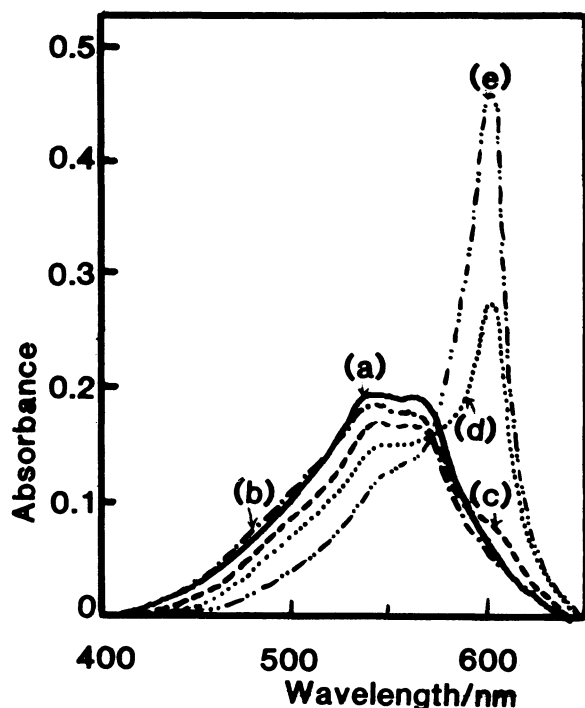


Fig. 2. Absorption spectra of the cast film of the merocyanine dye on the flexible electrode after soaking in the phosphate buffer (pH 7.0) for (a) 0 min, (b) 0.25 min, (c) 25 min, (d) 205 min, and (e) 352 min.

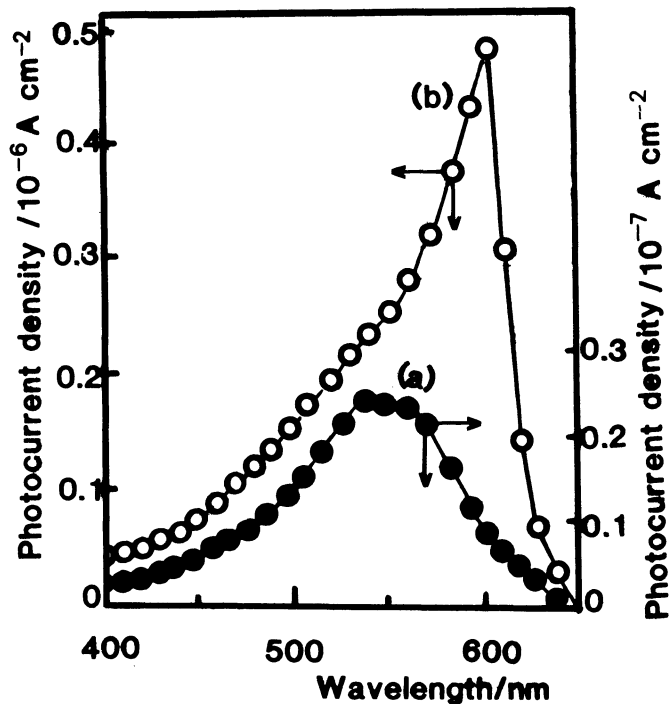


Fig. 3. Photocurrent spectra at the pigmented electrodes (a) without and (b) with the buffer treatment for 352 min. The spectra were taken in  $0.5 \text{ mol dm}^{-3} \text{ HCl}$  solution at  $0.3 \text{ V vs. SCE}$  at  $25^\circ\text{C}$ , and are normalized for an incident level of  $1 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$ .

buffer treatment has been found to harvest the light energy at longer wavelengths with higher quantum efficiency than that without the treatment. It has been found also that affinity between the dye film and the plastic electrode is strong enough to escape from destruction of the dye film on the plastic electrode even when the pigmented electrode is bent up to 6 mm of a radius of curvature. In addition, the dye molecules were not found to penetrate into the plastic electrode, probably due to presence of the ITO layer between the dye layer and the plastic film. These findings mentioned above may enable us to develop a light, flexible, and large-area electrode.

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#### REFERENCES

- 1) T. Moriizumi and K. Kudo, *Appl. Phys. Lett.*, **38**, 85 (1981).
- 2) F. Mizutani, M. Yoshiura, and K. Iriyama, *J.C.S. Chem. Comm.*, **1980**, 393.
- 3) K. Iriyama, F. Mizutani, and M. Yoshiura, *Chem. Lett.*, **1980**, 1399.
- 4) L.G.S. Brooker, G.H. Keyes, R.H. Sprague, R.H. VanDyke, E. VanLare, G. VanZandt, F.L. White, H.W.A. Cressmann, and S.G. Dent, Jr., *J. Amer. Chem. Soc.*, **73**, 5332 (1951).
- 5) S. Yasui, T. Shimamura, M. Funakoshi, and K. Iriyama, to be published.
- 6) K. Iriyama, Y. Ozaki, and M. Yoshiura, manuscript in preparation.

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