

# Photovoltaic Effect Based on Wet Poly(vinyl Alcohol) / Merocyanine Dye Junction

KAKU UEHARA, KENJI TAKAGISHI and MAKOTO TANAKA,  
*Department of Applied Chemistry, College of Engineering, University  
of Osaka Prefecture, Sakai, Osaka 591, Japan*

## Synopsis

The sandwich cell, Au/wet poly(vinyl alcohol) (PVA)/merocyanine (MD)/Au, based on the PVA/MD junction exhibited photovoltaic and rectifying effects. Forward dark current from the MD/Au electrode to the counter PVA/Au electrode through the cell was observed. The Au/MD electrode showed a positive photovoltage with respect to the PVA/Au electrode regardless of the direction of the incident light. It was suggested that a heterojunction barrier similar to the Schottky type formed at polymer/dye interface was responsible for the photo charge separation.

## INTRODUCTION

Organic thin film devices have received increasing attention from the vantage point of their potential to replace inorganic semiconductors in the development of large-area, easy-molding, lightweight, high-density, and inexpensive light-electricity conversion devices. While metal/organic Schottky barrier or inorganic-organic semiconductor *p-n* junction have been employed exclusively to fabricate organic solar cells,<sup>1</sup> organic-organic interfaces have received little attention.<sup>2-4</sup> As Tang<sup>4</sup> has reported, the maximum power conversion efficiency of the two-layer organic photovoltaic cell reached 15% for monochromatic light, which is higher than the most efficient metal-organic Schottky cell investigated over the last decade. Furthermore, the organic-organic system has many potential combinations to be examined. Our study focuses on fabrication of the photovoltaic sandwich cells based on the organic dye-polymer junction<sup>5,6</sup> to simulate the chlorophyll-protein complex in the green plant thylakoid membrane, which carries out a quite efficient charge separation using dilute solar energy at the initial stages of photosynthesis.<sup>7</sup> In this paper, we report the photovoltaic properties of the sandwich cell composed of wet poly(vinyl alcohol) (PVA) film with merocyanine dye, 3-carbomethyl-5-[(3-ethyl-2-(<sup>3</sup>H)-benzothiazolidene)ethylidene]-2-thionothiazolidine-4-one (MD, as shown in Fig. 1).

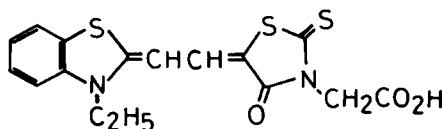


Fig. 1. Chemical structure of merocyanine dye (MD).

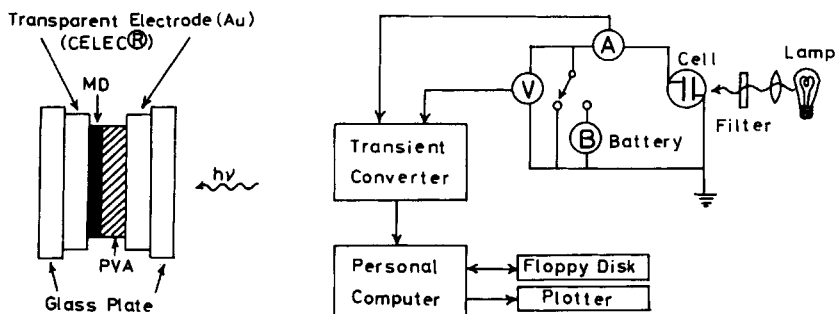


Fig. 2. The construction of the photovoltaic cell and the schematic diagram of an apparatus for the measurement.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA) film (VF-P, #7500) was donated by Kurarey Co. Ltd. The PVA film was cut to  $1 \times 1 \text{ cm}^2$  pieces, which were immersed in water for more than three days and stored in water vapor saturated atmosphere. The merocyanine dye MD (NK-2045) was supplied by Nippon Kanko Shikiso Co. Ltd., Okayama, Japan; and was used without further purification. Transparent electrodes "Celec," which were prepared by sputtering gold (Au) on polyester film, were supplied by Daicel Chemical Industries Ltd.

### Preparation of the Cell

The electrodes were washed clean with distilled water and dried with isopropyl alcohol vapor. MD was dispersed in chloroform by means of ultrasonic wave and then coated with a spinner on the surface of the transparent Au electrode. The wet PVA film was sandwiched between the MD-coated Au electrode and a counter Au electrode. As shown in Figure 2 the cell was held between two glass plates and compressed with clips under the dark water vapor-saturated atmosphere.

### Measurements

The photovoltaic effects of the cells were measured in the air at room temperature. Light was provided by a 300 W tungsten projector lamp with the neutral density filter and/or interference filters to adjust the light intensity and to select the wavelength. The direction of light irradiation is usually PVA/Au side (front irradiation).

## RESULTS AND DISCUSSION

### Current-Voltage Characteristics

The cells fabricated by the procedure described in the Experimental section exhibited rectifying and photovoltaic effects. Figure 3 shows the dark current-voltage characteristics for Au/PVA/Au and Au/MD/PVA/Au cells. As seen in Figure 3(a), the wet PVA film exhibited symmetrical nonlinearity.

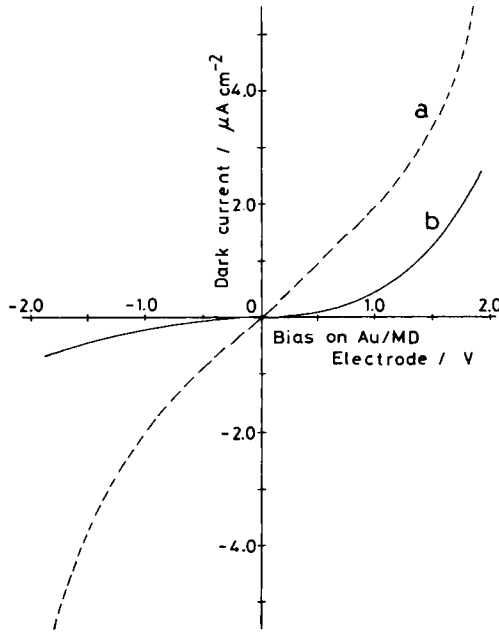


Fig. 3. The typical J-V characteristics in the dark: (a) wet PVA film; (b) MD/wet PVA cell.

The magnitude of the slope for  $-1.2 > V$  or  $V > +1.2$  range is about twice as large as that in the range of  $-1.2 < V < +1.2$ . From the dark J-V characteristics up to  $\pm 1.2$  V, the resistance of the wet PVA film is presumed to be  $5.0 \times 10^5 \Omega$ . And judging from the J-V characteristics, the wet PVA film is in ohmic or near ohmic contact with Au electrode.

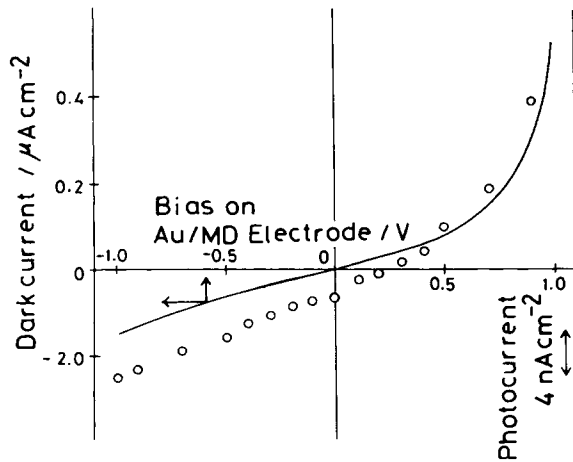


Fig. 4. The typical J-V characteristics: (○) under the light irradiation; (solid line) characteristics in the dark.

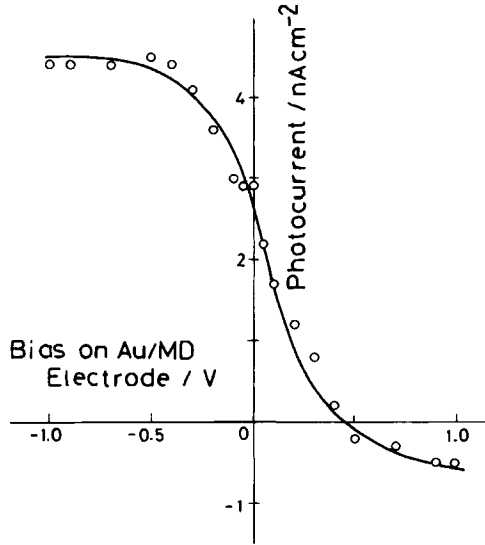


Fig. 5. The typical J-V curve under illumination subtracted by that under dark.

On the other hand, the cell exhibited the rectifying property as seen in Figure 3(b), which is forward when a positive voltage was applied to the Au/MD electrode. The initial current varies exponentially with voltage. The very small rectifying ratio (about 4 at 2.0 V) suggests that a weak barrier such as heterojunction would be formed within the MD layer at the interface of the PVA and MD.

Figure 4 shows the J-V curve under illumination through the KL-57 filter. As can be seen, at about 400 mV the direction of photocurrent was reversed, and in addition the photocurrent for the backward direction is larger than for the forward direction. In Figure 5, the J-V curve under illumination subtracted from that under dark is shown as the photocurrent V plot.

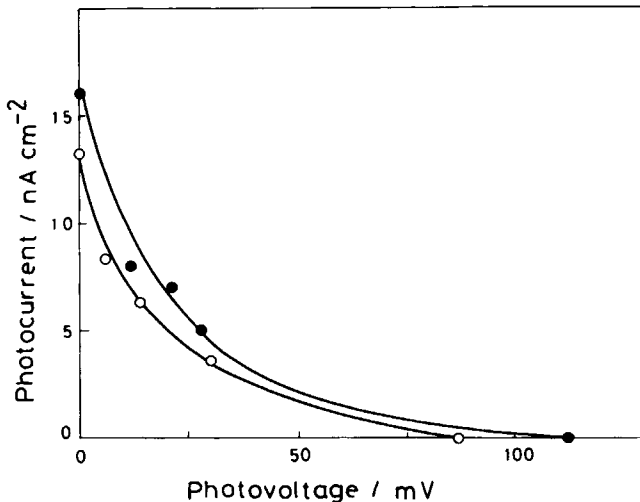


Fig. 6. J-V plot of the cell in the photovoltaic mode obtained by varying load resistance.

TABLE I  
Photovoltaic Device Properties of a Au/PVA/MD/Au Cell

Light	$I_T$ $\mu\text{W cm}^{-2}$	$J_{SC}$ $\text{nA cm}^{-2}$	$V_{OC}$ $\text{mV}$	$FF$ $(\times 10^2)$	$\eta'$ $\%(\times 10^5)$
With KL-57	150	16.0	112	7.8	9.3
Without KL-57	500	13.2	87	9.5	2.2

### Conversion Efficiency

The power curve of a cell under illumination was plotted by measuring the photocurrent in use of a variable load resistor from 10 K $\Omega$  to 10 M $\Omega$ . Figure 6 shows the power curves under monochromatic and white light. Table I shows the device parameters of the cells. The fill factors ( $FF$ ) of the cell defined by Eq. (1) are  $7.8 \times 10^{-2}$  for the monochromatic light and  $9.5 \times 10^{-2}$  for the white light, respectively.

$$FF = J_{mp} V_{mp} / J_{SC} V_{OC} \quad (1)$$

$J_{mp}$  and  $V_{mp}$  are the current density and voltage at the maximum-power point. With each of them, the  $FF$  is very small, and the power curves deviate extremely from that of ideal solar cell. This deviation presumably results from the large internal resistance and the high trap density of the present cells. The power conversion efficiencies of the present cells,  $\eta'$ , given by Eq. (2) are also very low.

$$\eta' = J_{SC} V_{OC} FF \times 100 / I_T \quad (2)$$

$I_T$  is the transmitted light intensity through the electrode. Nevertheless, the light intensity is larger than the monochromatic light, as shown in Table I, the values of  $J_{SC}$  and  $V_{OC}$  without a KL-57 filter are smaller than those with a KL-57, differing from the fill factor.

### Photoresponse of the Cells

An Au/MD electrode always generated a positive photovoltage against the counter PVA/Au electrode regardless of the direction of light irradiation. This behavior excludes the common Dember effect, since the sign of the photovoltage must depend on the direction of irradiation according to the Dember effect. Figure 7 shows a typical time profile of the open circuit photovoltage,  $V_{OC}$  for the cell. The situation of trap density and the dielectric properties of the dye and/or polymer layer may contribute to the time profile behavior for the emergence and decay of  $V_{OC}$ .

Figure 8 shows the response of short circuit photocurrent  $J_{SC}$  for the cell. Curve (a) is for the light incident through the Au/Dye electrode and curve (b) is for the PVA/Au electrode. The transient photocurrent behavior will be the characteristics of cells dominated by trapping effects. But the reverse spike

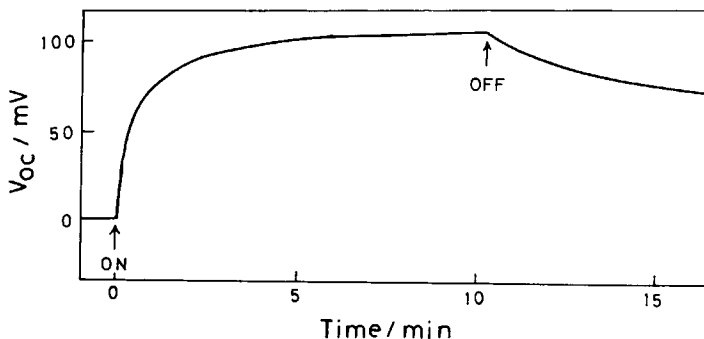


Fig. 7. A typical time profile of open circuit photovoltage by the illumination at 570 nm for light incident on MD side.

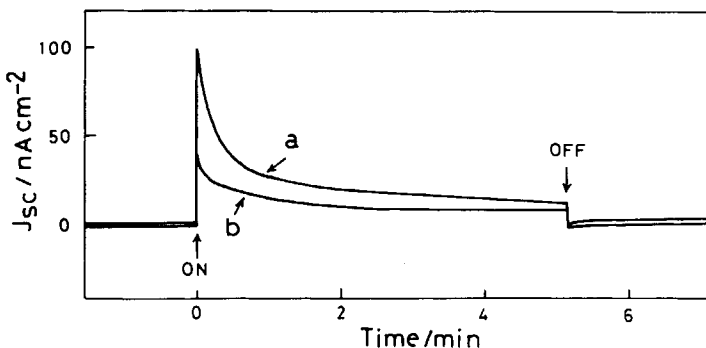


Fig. 8. A typical time profile of short circuit photocurrent by the illumination at 570 nm: (a) for light incident on MD side; (b) for light incident of PVA side.

current, which was given by a device such as photoelectrolytic condenser, was not observed.

### Dependence of the Photocurrent and Photovoltage on the Incident Light Intensity

Figure 9 shows the changes in  $J_{SC}$  and  $V_{OC}$  and a function of incident light intensity. Relative light intensity 100% stands for  $1.5 \text{ mW cm}^{-2}$ . Two instances were given for 570 nm light of large absorbance and 740 nm light of small absorbances, respectively. Both  $J_{SC}$  and  $V_{OC}$  increase almost linearly with light intensity. The slope for the 570 nm light is a little larger than that for the 740 nm light although the slopes are very small. Since it is known that the number of carriers increases linearly with the number of photons, the above results suggest that the trap density is high and recombination of carrier occurs frequently.

### Action Spectra

Figure 10 shows the absorption spectrum of MD coated on the transparent Au electrode (a) and that of an MD-dyed PVA film prepared by immersing into aqueous MD solution (b). The action spectra of  $J_{SC}$  for front- and

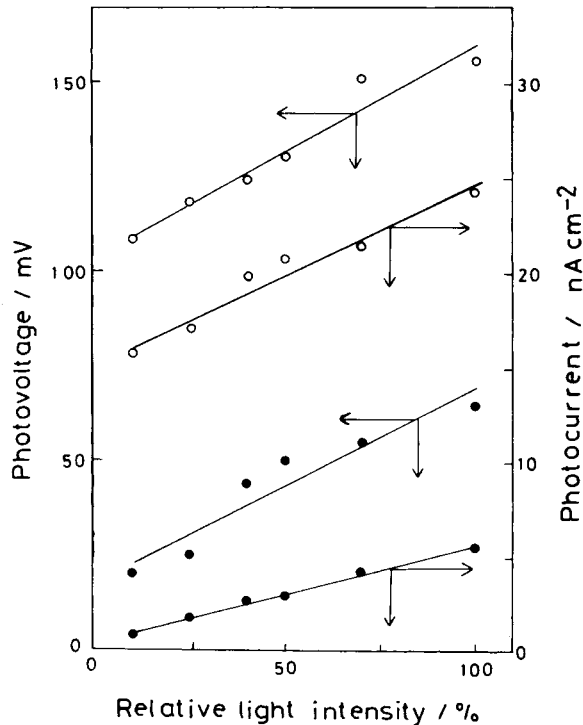


Fig. 9. Light intensity dependence of short circuit photocurrent and open circuit photovoltage: (○) irradiation at 570 nm,  $I = 1.5 \text{ mW cm}^{-2}$ ; (●) irradiation at 740 nm,  $I = 0.6 \text{ mW cm}^{-2}$ .

backside irradiations are also shown in Figure 10(c, d).  $J_{SC}$  was normalized for the intensity of light. The photocurrent and absorption are essentially in close correlation regardless of the incident light direction. MD coated on the Au electrode has two absorption maxima at 520 and 580 nm. The absorbance at 520 nm is greater than that at 580 nm. When the light is irradiated through the PVA/Au electrode, the action spectrum gives only a maximum around 580 nm and there is no maximum near 520 nm. This suggests that the 570 nm form of MD is much more effective for the light-electric conversion than the other form of MD which absorbs the light at around 520 nm. The active form of the dye is not yet characterized.

As the MD is a water-soluble dye, PVA film can be dyed uniformly by immersion in aqueous solution of MD. The resultant MD-dyed PVA (MD-PVA) film absorbing at 540 nm was used for the cell: Au/MD-PVA/Au. However, this cell did not show any photoresponse. The poor effectiveness of the 520 nm monochromatic light irradiated through the PVA-Au electrode may be ascribed to the filter effect of the dye molecules dispersed within the PVA film.

#### A Possible Mechanism for the Photovoltaic Effect

The experimental results of the Au/MD/PVA/Au photovoltaic cells may be understood on the basis of a band model. It is well known that MD dye behaves as a “*p*-type” semiconductor and makes ohmic contact with Au,

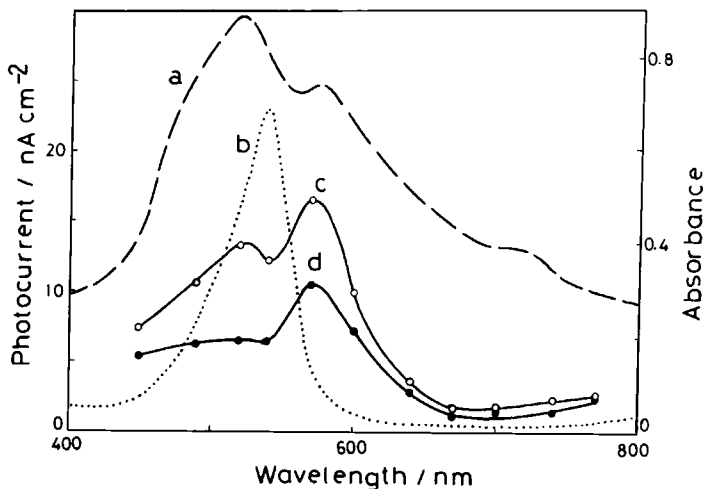


Fig. 10. Action spectra of short circuit photocurrent (solid line) and absorption spectra of MD coated on Au film (broken line) and of the dyed PVA film by MD aqueous solution (dotted line); (○) for light incident on the MD side; (●) for light incident on the PVA side.

which has a relatively high work function, while the wet PVA film makes ohmic or near ohmic contact with Au electrodes. The conduction and valence band edges of MD are bent downward at the MD/PVA interface. A hetero-junction barrier similar to Schottky type may be formed at the junction of PVA and MD. When the light is turned on, the excitons generate in the MD layer. The excitons generated in and diffused to the barrier dissociate into carriers with a defined efficiency. In agreement with such a view, the potential of PVA side becomes negative on light irradiation. The carrier transport in PVA is still ambiguous. It may be possible that electrons flow through PVA by a hydrogen-transfer mechanism proposed by Shigehara et al.<sup>8</sup> However, the ionic conduction by ionic species such as  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  which resulted from water in PVA cannot be excluded. Further investigation is required for the elucidation of the conduction mechanism in PVA.

## CONCLUSIONS

The cells fabricated using wet PVA and MD exhibited a photovoltaic and rectifying effects. This behavior is due to a barrier formed at the wet PVA/MD interface. The barrier is like Schottky type. It is noteworthy that the polymer/dye interface is important for the charge separation. The cell using the PVA film which was dyed uniformly in an MD aqueous solution does not show any response to the light. From the photocurrent action spectra, the form of MD which absorbs the light of around 570 nm showed the largest photocurrent. It is of interest that the specific form of a dye is effective for light-electron conversion.

This work was partially supported by a Grant-in-Aid on Special Project Research for "Organic Thin Films for Information Conversion" No. 60211026 from the Ministry of Education, Science and Culture, Japan. The gifts of transparent electrode "Celec" from Daicel Chemical Industries, Ltd. and PVA film from Krarey Co., Ltd. are gratefully acknowledged.



**References**

1. G. A. Chamberlein, *Solar Cells*, **8**, 47 (1983).
2. D. Kearns and M. Calvin, *J. Chem. Phys.*, **29**, 950 (1958).
3. K. Yamashita, Y. Matsumura, Y. Harima, S. Miura, and H. Suzuki, *Chem. Lett.*, 489, (1984).
4. C. W. Tang, *Appl. Phys. Lett.*, **48**, 183 (1986).
5. K. Uehara, T. Yoshikawa, M. Katoh, M. Tanaka, N. Isomatsu, and M. Hiraishi, *Chem. Lett.*, 489, (1984).
6. K. Uehara, T. Iwai and M. Tanaka, *Chem. Express*, **1**, 137 (1986).
7. R. S. Knox, *Topics in Photosynthesis*, vol. 2, edited by J. Baker, Elsevier, New York, 1977, p. 55.
8. K. Shigehara, M. Nishimura, and E. Tsuchida, *Electrochim. Acta*, **23**, 855 (1978).

Received January 22, 1987

Accepted July 30, 1987