CHEMISTRY LETTERS, pp. 1499 - 1502, 1984. © The Chemical Society of Japan 1984

PHOTOVOLTAIC SANDWICH CELLS BASED ON THE CHLOROPHYLL A / WET POLY(VINYL ALCOHOL) JUNCTION

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A new type of photovoltaic device was made by contacting chlorophyll a (chl) layer with wet poly(vinyl alcohol) (PVA) film between two electrodes to give a cell such as Au/chl/PVA/Au. The cell showed a rectifying effect. It was suggested that the charge-separation upon irradiation of visible light might occur at the junction between chl layer and PVA film.

Green plants convert sunlight into electrochemical energy with a quite high efficiency in their initial stage of photosynthesis. The desire to obtain an effective organic photovoltaic devices modeled on the photosynthetic process has led to the study of a large number of chlorophyll photovoltaic cells.1) These studies have demonstrated the possibility of employing a blocking contact (Schottky type barrier) formed at the junction between chlorophyll and a metal with a low work function. However, the attempts to obtain high power conversions are unsuccessful as yet.

Photosystem in plant is a highly organized pigment-protein complex which is embedded in thylakoid membranes. And protein in the membrane should play an important role. To study the effect of polymeric materials, we present here a new approach to the fabrication of organic solar cells, namely, the use of the junction between chl layer and wet PVA film. It might give an another way of studying efficient chl solar cells.

Chl was extracted from fresh green spinach and purified by the method of Iriyama et al.2) PVA film (VF-P, #7500) was kindly donated from Kurare Co., Ltd. Transparent electro-conductive films Celec® G- and K-series, which were prepared by spattering gold(Au) and indium-tin oxide(ITO) respectively on polyester, were supplied by Daicel Chemical Industries, Ltd. Chl was coated on the surface of the electrode by dropping and spreading 0.16 ml of acetone solution(6×10^{-4} mol dm^{-3}) and by evaporating acetone in vacuo. PVA film was wetted well by immersing into water for more than one day and sandwiched between the chl-coated electrode and a counter electrode. The cell was held tightly between two glass plates with clips as shown in Fig. 1. The cell setup was stored in dark at room temperature over saturated water vapor before use. The time-dependent absorption spectra of chl in the cell assembly after contacting with wet PVA film showed that absorption maximum

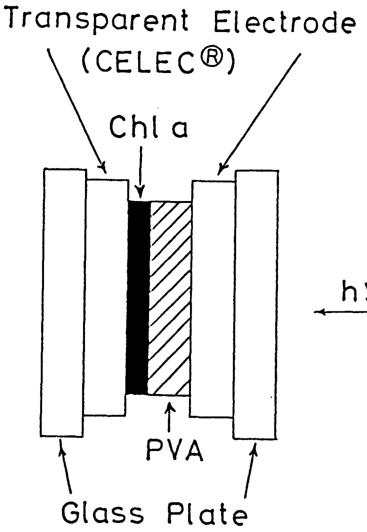

Fig. 1. Fabrication of chl/PVA cell.

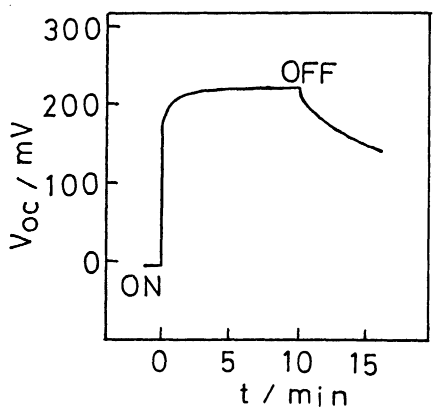

Fig. 2. Open circuit photoresponses for Au/chl/PVA/Au cell under the filter cut light by VR-61 and IRQ-80 (610<λ<800 nm).

at 670 nm shifted to 740 nm indicating the aggregation of chl to give polycrystalline chl dihydrate $(\mathrm{chl}\cdot 2H_2O)_n$.[3] The cell to be analyzed was positioned in a steel shield box. Light was provided by a 300 W tungsten projector lump with glass filters, Toshiba VR-61 and IRQ-80, or interference filters. Voltages and currents were measured with a Hokuto HA-301 potentiostat/galvanostat and a Toa PM-18R DC microvolt ammeter.

Figure 2 shows an example of open circuit photoresponses for a Au/chl/PVA/Au cell. The illuminated Au/chl electrode always generated a positive photovoltage against the counter Au electrode. And when the light was off, it was gradually decreased to the initial dark potential. Photocurrent passed from the counter Au to the Au/chl through the cell. Figure 3 shows two typical time profiles of short circuit photocurrents for the cell: (a) continuous irradiation for 10 min; (b) repetition of short-term irradiation by means of a chopper (four cycles photo-on-off per 10 s). When the light was on, the cell exhibited a fast and large transient spike which decreased gradually to a steady state in about 10 min illumination. This transient spike was observed in the short circuit signal and it might be caused by a current characteristic of PVA as an insulator. The sharp spike was reproducible upon repeated short-term light-on-off. Table 1 shows some examples of open circuit photocurrent (I_{sc}) given by using two different kinds of transparent electroconductive films for chl-coated and counter electrodes. V_{oc} was given as the difference of dark-potential and maximum illuminated-potential. I_{sc} was given as the photocurrent measured after 10 min illumination onto the cell in order to avoid

Table 1. Photovoltage (V_{oc}) and photocurrent (I_{sc}) for chl/PVA cells

Chl-coated electrode	Counter electrode	V_{oc}/mV	I_{sc}/μA cm^{-2}
ITO	ITO	254	0.016
ITO	Au	287	0.167
Au	Au	227	0.096

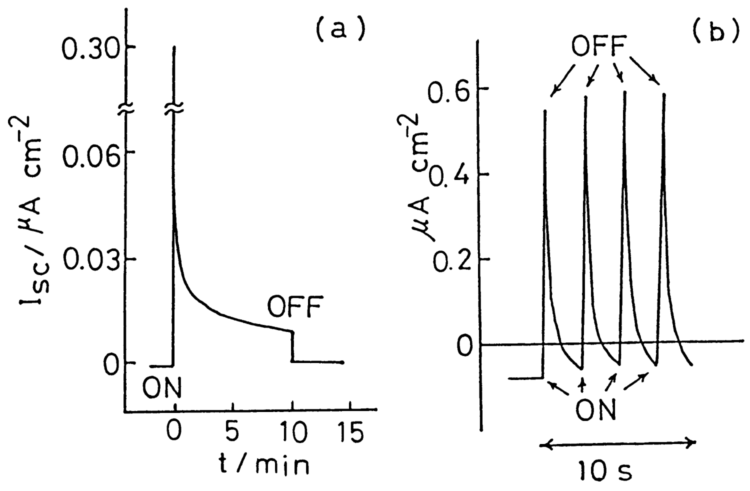

Fig. 3. Typical time profiles of short circuit photocurrent for Au/chl/PVA/Au cell by the illumination of 610<λ<800 nm light.
(a) continuous irradiation, (b) repetition of short-term irradiation by means of a chopper.

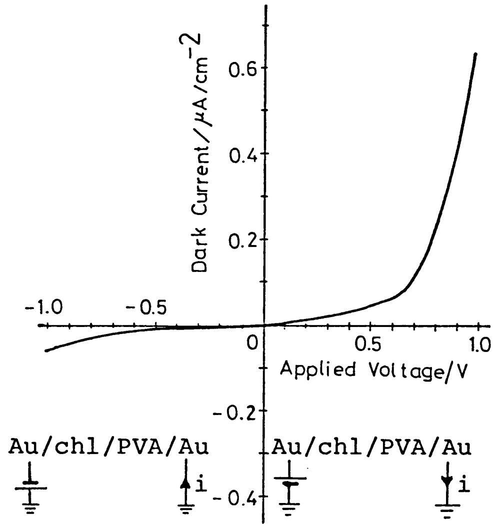

Fig. 4. Dark current-voltage characteristics of Au/chl/PVA/Au cell.

the transient current. Figure 4 shows dark current-voltage characteristics for the Au/chl/PVA/Au cell. The cell exhibited a rectifying effect. Forward current flowed from the chl-coated Au electrode to the counter Au electrode through the cell. Similar rectifying effect was also observed for other two types of cell shown in Table 1. Internal cell resistance was evaluated as $\approx 10^{-7}$ Ω cm from the values of applied voltages and dark currents.

The photocurrent of the present metal/chl/PVA/metal photovoltaic cells depended very much on the amount of water absorbed in the PVA film. Water may enhance the conductivity of PVA film. The conduction through PVA film may proceed by an ionic mechanism although the electron carrier species are not identified as yet. Tsuchida et al.[4)] have reported about the enhanced electron exchange reaction between Fe(II) and Fe(III) by aqueous PVA. Furthermore, it has been reported that water molecule acts as a ligand for chl to form hydrated aggregates and thereby enhances the photocharge separation.[5)]

The sign of the photovoltage of the Au/chl/PVA/Au was such that the Au/chl electrode was always positive. Figure 5 shows the photocurrent-voltage characteristics of the cell. For this experiments, chl was coated on 4 cm^2 square Celec® G-B from petroleum ether solution by means of a spinner, which was divided into four square pieces to make independent measurements like that shown in Fig. 5. The optical density of coated chl on the film was 1.2(λ_{max}= 743 nm; thickness $\approx$120 nm). The curve was obtained by varying the load resistance at a constant light intensity adjusted with interference filter KL-74(λ_{max}= 743 nm) and VR-61 filter. The maximum power output from this cell through the resister was about 1.7×10^{-9} W cm^{-2}. The incident light power was about 1.6×10^{-5} W cm^{-2} (after correction for the optical density of PVA/Au film). The power conversion efficiency at this light level was in the order of 10^{-2}% (fill factor= 0.39).

The Au/chl/PVA/Au cell had remarkable photovoltaic properties as described above and its general features are given by the followings: (i)The positive potential shift

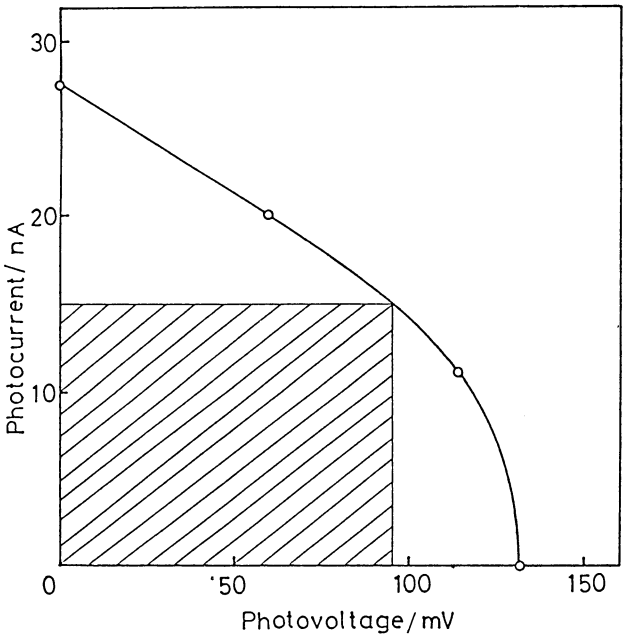

Fig. 5. Photocurrent-photovoltage characteristics of Au/chl/PVA/Au cell.

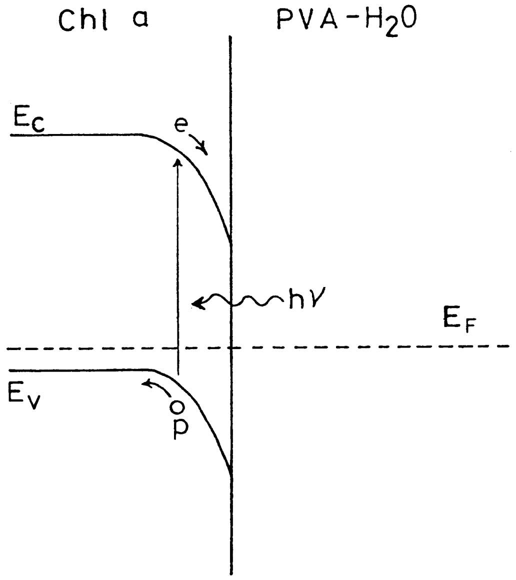

Fig. 6. A possible potential-energy diagram of the chlorophyll a / wet poly(vinyl alcohol) junction.

was observed for chl-coated electrode with respect to the counter electrode upon light irradiation, (ii) The time profile of the photocurrent showed a sharp spike pattern, and (iii) The cell exhibited a dark rectification behavior. Furthermore, it was observed that the efficiency for backside irradiation onto the cell (hν→Au/chl/PVA/Au) was less effective than for forward irradiation (hν→Au/PVA/chl/Au). These findings suggest that a blocking contact is formed at the chl/PVA and is effective in producing charge carriers. The conduction- and valence-band edges of chl, a p-type semiconductor, are bent downwards at the chl/PVA interface under short circuit conditions as shown in Fig. 6. The Au/chl interface is less photoactive because the contact at the junction is ohmic or near ohmic.[1c] It is interesting to compare our chl/PVA blocking contact with the n-Si/Pt/polypyrrole photoanode cell reported by Skotheim and Lundström[6] and with organic p-n junction formed at 5,10,15,20-tetraphenylporphinatozinc(II)/5,10,15,20-tetra(3-pyridyl)porphyrin interface pointed out by Yamashita et al.[7]

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(Received June 9, 1984)