A Photoelectrochemical Study of Polyacetylene, $(CH)_x$

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Synopsis. The photoelectrochemical behavior of *p*-type semiconducting *trans*-$(CH)_x$ film in the presence of *N,N'*-dimethyl-4,4'-bipyridinium as the solution species is described. The spectral response of the photocurrent shows a mismatch with the absorption spectrum, and the quantum yield ($\approx 10^{-3}$) of the charge flow is extremely low. It is assumed that $(CH)_x$ film has a high trap density and that the lifetime of the photogenerated hole is limited by trapping and recombination in the space-charge region.

In recent years, there has been a considerable interest in the electrical and optical properties of polyacetylene, $(CH)_x$, film as a new class of semiconducting material.[1-6] A $(CH)_x$-sodium polysulfide solution photovoltaic cell has been fabricated as an active photoelectrode for a photoelectrochemical cell.[7] Although Chen *et al.* mentioned that the $(CH)_x$ photocathode exhibited significant photoresponse with an open circuit voltage, $V_{oc} \approx 0.3$ V, and a short circuit current, $I_{sc} \approx 40$ μA/cm^2, under illumination of approximately 1 sun,[7] the photoresponse ($V_{oc} \approx 60$ mV, $I_{sc} \approx 1$ μA/cm^2) in our work was very low. These results suggest that, in order to use the $(CH)_x$ as an active photoelectrode for a photoelectrochemical cell, it is of primary importance to characterize its general photoelectrochemical behavior before any modification experiments are performed. The studies reported here concern the basic photoelectrochemical properties of the *trans*-$(CH)_x$ film in the presence of *N,N'*-dimethyl-4,4'-bipyridinium (MV^{2+}) as the solution species.

Experimental

The preparation of the *trans*-$(CH)_x$ film has been described elsewhere.[8] The film was about 0.1 mm thick. The conductivity of the film was found to be about 10^{-6} Ω^{-1} cm^{-1}, as determined by the standard four-probe van der Pauw technique.[9] The ohmic contact with a thin copper sheet was obtained by the use of Electrodag on the shiny side of the $(CH)_x$ film. The preparation of the $(CH)_x$ working electrode was done according to Chen's method.[7]

Photocurrent measurements were performed under potentiostatic conditions with a home-made potentiostat.

The light source used in the study of the photoelectrochemical effect was a 100-W high-pressure mercury lamp with a glass filter ($\lambda \leq 430$ nm cut-off). A water filter with a 10-cm optical pathlength as a heat-absorbing filter was employed. Chemical actinometry for 436-nm-wavelength light, obtained by combination with a KL-43 filter, was carried out using the potassium ferrioxalate system. The measurement of the action spectrum of the photocurrent was done by the lock-in (NF Model LI-574) technique using a modulation of the light beam with 8 Hz. As a light source in this case, a Xe 500-W lamp was used, while a grating monochrometer (Nikon G-250) was employed for the wavelength selection.

Reagent-grade chemicals were used without further purification. All the solutions were deoxygenated for at least 30 min with purified nitrogen before each experiment. All the experiments were carried out with the solution under nitrogen without stirring.

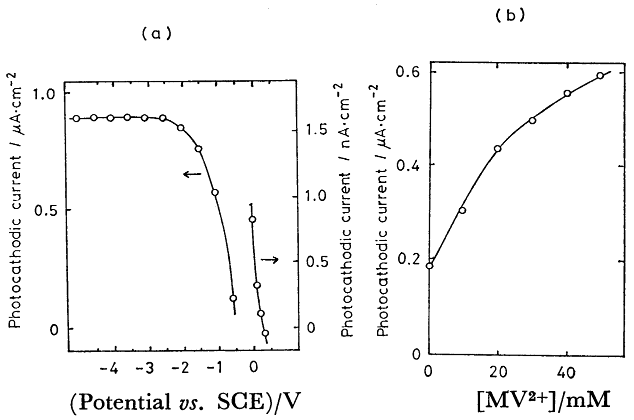

Fig. 1. (a) Steady-state photocurrent *vs.* electrode potential for 20 mM MV^{2+} in 1 M KCl (pH 5) at *trans*-$(CH)_x$ electrode; (b) Steady-state photocurrent as a function of concentration of MV^{2+} (1 M KCl, pH 5, $U_{SCE} = -1.0$ V).

Results and Discussion

Cyclic-voltammetric curve revealed that the $(CH)_x$ film did not react with MV^{2+} in the dark at all. Figures 1(a) and (b) show the steady-state photocurrent-voltage characteristic and the dependence of the signal on the MV^{2+} concentration respectively. The results can be qualitatively explained in terms of the p-type semiconducting properties of the $(CH)_x$ film. The cathodic photocurrent indicates that MV^{2+} acts as a primary acceptor of the electron as the minority carrier ejected from the $(CH)_x$ into the solution and can be attributed to the reduction of MV^{2+} to the purple $MV^{\cdot +}$, as evidenced by the blue-purple color streaming from the $(CH)_x$ film surface at $U_{SCE} \leq -1.5$ V. This fact suggests that the lower edge of the $(CH)_x$ conduction band is positioned at energies above the standard redox potential (-0.7 V *vs.* SCE) of $MV^{2+}/MV^{\cdot +}$.[10] Figure 1(b) shows the observation of the signal in the absence of MV^{2+} as well. The electron acceptor in this case remains unidentified, but dissolved oxygen gas as an impurity is a possible candidate, because O_2 can mediate the transfer of the conduction-band electron across the $(CH)_x$ film-solution interface. The onset potential ($U_{SCE} \approx 0.4$ V) of the photocurrent, which approximately corresponded to the flat-band potential for the $(CH)_x$ electrode, was almost independent of the solution pH (1—13), and the signal decreased with the solution acidity when U_{SCE} was kept constant. When a solution containing sodium polysulfide (20 mM as Na_2S_2) and 1 M (mol dm^{-3}) KCl at pH 11.6 was used,[7] the photo-

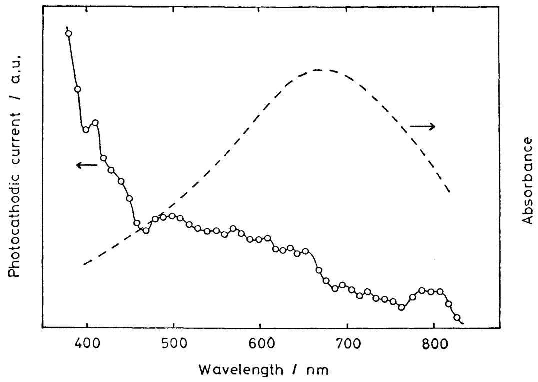

Fig. 2. Spectral response (in arbitrary units) of *trans*-$(CH)_x$ electrode in 20 mM MV^{2+}+1 M KCl aqueous solution (pH 5).
Dashed curve indicates absorption spectrum of *trans*-$(CH)_x$ with about 1 μm in thickness.

current was lower (≈0.27 μA/cm² at $U_{SCE}=-1.0$ V) than that of the 20 mM MV^{2+} system at pH 5 (≈0.45 μA/cm² at $U_{SCE}=-1.0$ V). This lower photocurrent may be mainly caused by an absorbance of the polysulfide solution used, and we may conclude that, in the polysulfide electrolyte, $(CH)_x$ does not exhibit the significant photoresponse previously reported.[7]

In Figure 2 the spectral response of the $(CH)_x$ electrode is shown. The data on the vertical axis were obtained by dividing the photocurrent at a certain wavelength by the number of photons incident on the electrode. It can be seen that the spectral response of the photocurrent shows a mismatch with the absorption spectrum of the $(CH)_x$ film, which exhibits an absorption maximum at 670 nm.[11] Similar behavior has been observed for the solid-state $(CH)_x$ Schottky junction.[12] The threshold of the photocurrent response is observed at about 830 nm (≈1.5 eV), in agreement with the direct-band gap calculated from the optical studies of the $(CH)_x$ film.[1] The anticorrelation between the action and the absorption spectrum indicates that the light absorbed on the front suface of the $(CH)_x$ film is not effective in creating free-charge carriers. In effect, most holes generated on the front surface are not long-lived enough to diffuse into the space-charge layer, while holes generated within the bulk have a finite probability of transiting the space-charge layer to be registered as carriers in the external circuit. The rate of charge generation at a certain distance, x, from the front surface is proportional to $\exp(-kx)$, where k is the absorption coefficient of the $(CH)_x$ film (for example, $k_{670}\approx 2\times10^5$ cm^{-1} [1]). Detailed studies of the photovoltaic response for p-$(CH)_x$: n-CdS heterojunction have implied the existence of a meta-stable trapping state 0.9 eV below the conduction band of the $(CH)_x$ film.[6] Therefore, the anticorrelation may be explained by assuming that the $(CH)_x$ film has an excessively high trap density; if the penetration depth of the light ($\lambda \leq 600$ nm) is large, the trapping of the photogenerated holes may be insignificant compared to the case of about a 670 nm-wavelength light corresponding to the absorption maximum of the $(CH)_x$ film. The quantum yield of the charge flow under the 436-nm-light irradiation was extremely low, being 1×10^{-3} at $U_{SCE}=-1.0$ V in the 20 mM MV^{2+} +1 M KCl aqueous solution (pH 5). Furthermore, the light-intensity dependence of the photocurrent varied with the applied potential; the light-intensity exponent for the photocurrent was less than unity and increased from 0.8 to 0.9 as $-U_{SCE}$ increased from 0.5 to 3.0 V. These results may be related to the recombination or trapping of the photogenerated holes in the bulk of the $(CH)_x$ film, which arises from the high trap density and which well limits the photocurrent to a significant level, if we consider that an increase in the electric field in the space-charge layer would cause the photogenerated holes to have an increasing chance of transiting the space-charge layer before being trapped.[13]

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13) The AsF_5-doped *trans*-$(CH)_x$ film with 8.4×10^{-3} Ω^{-1} cm^{-1} exhibited 5×10^{16} and 2.5×10^{18} cm^{-3} as the ionized acceptor concentration (N_A) and the trap density (N_T), respectively.[14] Accordingly, it may be reasonable to assume $N_A\approx10^{15}$ cm^{-3} for the present $(CH)_x$ film with 10^{-6} Ω^{-1} cm^{-1}. Then, about 10^4 Å as the space-charge layer width under the band bending of about 1 eV can be calculated, when $\varepsilon\approx10$ is taken as the dielectric constant. In this case, most of the absorption maximum-photons ($k_{670}\approx 2\times10^5$ cm^{-1}) incident on the $(CH)_x$ film would be absorbed within 10^3 Å of the front surface, and most of the photogenerated holes would be not long-lived enough to transit the space-charge layer with a 10^4 Å width, due to the trapping by the high-trap density (probably $N_T>2.5\times10^{18}$ cm^{-3}). This may lead to the absence of any parallel effect for the photocurrent signal, as is shown in Fig. 2.

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