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EFFECT OF DOPING OF ClO_4^- ON THE PHOTOELECTROCHEMICAL PROPERTIES OF POLYACETYLENE

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The effect of electrochemical doping on the photoelectrochemical properties was studied for p-type semiconducting trans-polyacetylene. The magnitude of photocurrent, the response spectrum, the electrode capacitance and resistance were measured and discussed in terms of the effect of the doping.

Polyacetylene has attracted considerable attention for its unique electrical properties and its capacity to be manufactured at a moderate price. The conductivity of polyacetylene could be widely varied over twelve orders of magnitude by various methods of doping.[1-4] Only a few studies on photoelectrochemical properties of semiconducting polyacetylene have been reported. Chen et al.[5] first reported the current voltage characteristics and photoresponse spectrum for undoped polyacetylene in a solution of sodium polysulfide. They also demonstrated first a photoelectrochemical cell of polyacetylene constructed with a platinum wire. Yamase et al.[6] described the photoelectrochemical behavior in the presence of N,N'-dimethyl-4,4'-bipyridinium (MV^{2+}) as solution species. The present study demonstrates the effect of electrochemical doping on the photoelectrochemical properties such as the magnitude of photocurrent, the response spectrum and carrier density.

The polyacetylene films used were a generous gift from Showa Denko Co. Ltd. The films (ca. 0.1 mm thick and 93% trans content) were prepared by the method reported by Shirakawa and coworkers.[7] The shiny side of the film is connected to a copper lead by using Ag-paste. The working electrode was prepared so as to expose only the outermost fibrils to the electrolyte.[5] Electrochemical doping was performed in an aqueous solution of $LiClO_4$. The degree of anion incorporation was controlled by varying the concentration of $LiClO_4$ (0.1-1.0 mol/dm^3), the electrode potential (2-8 V vs. SCE) and the loading period (0-30 min).

Photocurrent was measured in an aqueous solution of 0.1 or 0.5 mol/dm^3 $LiClO_4$ with a homemade potentiostat, a saturated calomel reference electrode, and a platinum wire auxiliary electrode. The polyacetylene working electrode were irradiated with a 400 W Xe-lamp through a monochromator. As an electron acceptor in the solution 1 mmol/dm^3 of MV^{2+} was used. To deoxygenate the solution, nitrogen gas was passed through before and during each experiment. The capacitance and

resistance of the electrodes were measured through a 1 kHz AC-bridge circuit.

Figure 1 represents the cyclic-voltammograms for the doped and undoped polyacetylenes. Under illumination the greater cathodic photocurrent is observed for the electrochemically doped polyacetylene electrode. The photocurrent quantum efficiency is on the order of 0.01% for the doped one. However, it will be increased when the film is thinner and the fibrils are more oxposed.[5] At the cathodic potential of -1.0 V, the photocurrent decayed at a rate of roughly 10^{-3} s^{-1}. The decay corresponds to disdoping of the ClO_4^- ions incorporated in the film.

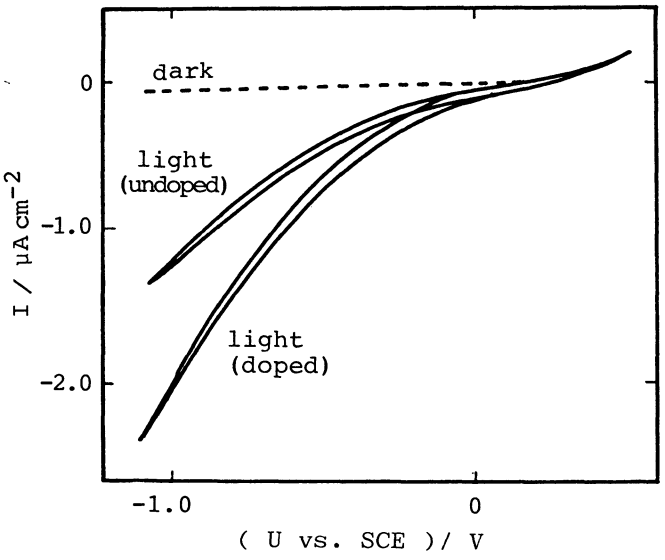

Fig. 1. Cyclic-voltammograms for doped and undoped polyacetylene in 0.5 mol/dm^3 $LiClO_4$. Sweep rate 50 mV/s, light intensity 0.3 W/cm^2, wavelength 500 nm.

The corrected response spectrum of the photocurrent of the electrochemically doped polyacetylene is shown in Fig. 2. The spectrum for the undoped polyacetylene was essentially the same in shape as that for the doped one. This coincides with a report on the open-circuit photovoltaic response[8] that the threshold is independent of the doping level. The threshold of the photocurrent response was found to be 950 nm,

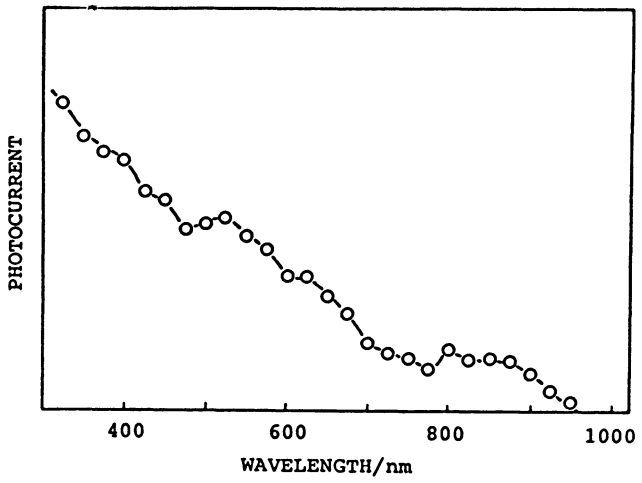

Fig. 2. Corrected response spectrum of photocurrent for doped polyacetylene at a fixed potential (-0.4 V vs. SCE) in 0.1 mol/dm^3 $LiClO_4$ solution.

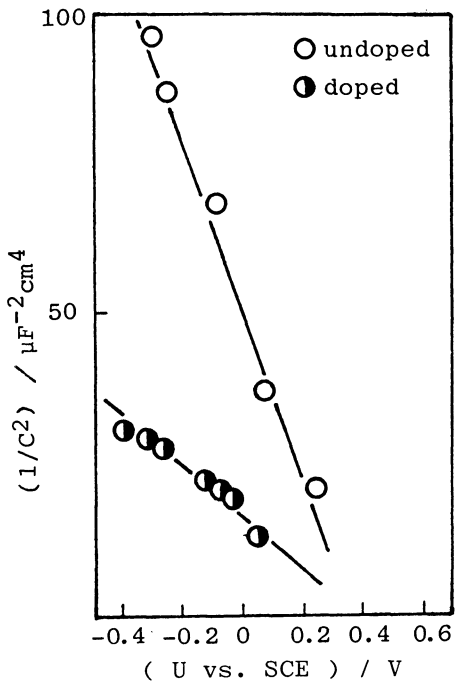

Fig. 3. Mott-Schottky plot for polyacetylene electrodes in acetonitrile solution of 0.1 mol/dm^3 $LiClO_4$.

which is a longer wavelength than that (830 nm) of a previous photoelectrochemical study.[6] The broad peak observed at 850 nm may correspond to that observed in the photoconductivity response which have been tentatively attributed to dissociated weakly-bound Wannier excitons.[8]

Figure 3 represents the Mott-Schottky plots for undoped and electrochemically doped polyacetylene electrodes. The decrease of the slope with doping means the increase of carrier density. Assuming $\varepsilon = 10$ as the dielectric constant, the carrier density is calculated to be 9×10^{16} and 2.6×10^{17} cm^{-3} for the undoped and doped polyacetylene, respectively. The flat band potentials estimated from the plots are about 0.4 V for both electrodes. This value roughly agrees with the onset potential of the cathodic photocurrent shown in Fig. 1. Although the mechanism of the transport of the carrier is not totally clear, the above observations suggest that the photoelectrochemical characteristics of the doped polyacetylene electrode are similar to those of inorganic semiconductor electrodes.

The series resistances and electrode capasitances were measured for the electrodes containing various amounts of dopant. The photocurrents for these electrodes were also measured. In Fig. 4, the reciprocal of the capacitance (1/C) and the ratio of the photocurrent of the doped polyacetylene to that of the undoped one (I_{pd}/I_{po}) are plotted as a function of the reciprocal of the resistance (1/R). The conductivity, which corresponds to 1/R, is generally expressed by the product of carrier density and mobility of carrier. The carrier density is proportional to C^2 as stated above. Therefore, if the mobility of carrier does not change with

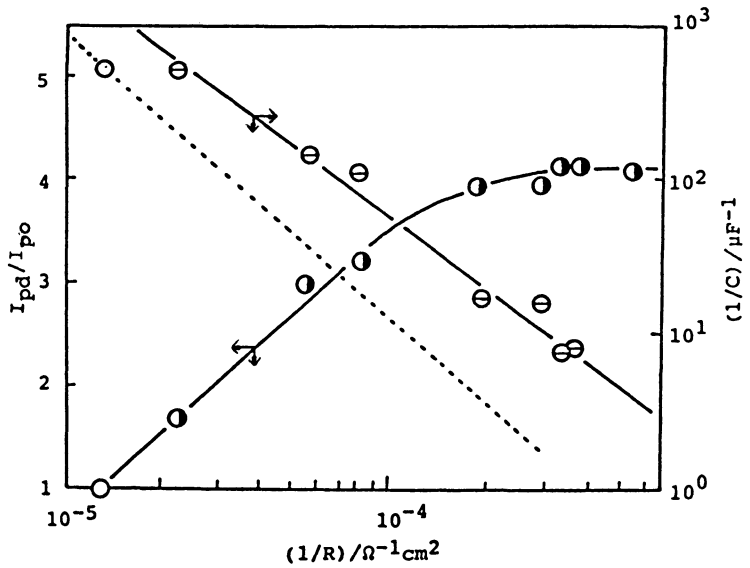

Fig. 4. Plot of relative photocurrent and the reciprocal of electrode capacitance as a function of the reciprocal of series electrode resistance per unit area. The photocurrent measured by using cyclic-voltammetry are normalized to that of undoped polyacetylene.

doping, the logarithm of 1/R will be proportional to the logarithm of 1/C with a coefficient of -2 as shown by the dotted line in Fig. 4. The log-log plot of 1/C vs. 1/R for the doped polyacetylene shows a straight line and the experimental data were located on the right side of the dotted line. This observation suggests that electrochemical doping alters the mobility of carrier as well as the carrier density.

As shown in Fig. 1, the photocurrent increases with cathodic potential. This indicates that the increase of cathodic potential prevents the recombination of the photo induced electron-hole pairs in this potential range. That is, the frequency of the recombination decreases with an increase of the electrode polarization. Therefore, the increase of the photocurrent by doping is attributed to the decrease of the frequency of the electron-hole recombination. This is also shown by the plot in Fig. 4, where photocurrent increases with a decrease of the electrode resistance caused by doping of ClO_4^-. The experimental results are explained by the fact that the increase of the electric field-gradient of depletion layer with the carrier density causes less frequent recombination of photoinduced electron-hole pairs. When the value of 1/R reaches about 10^{-4} $\Omega^{-1}cm^2$ the increase of photocurrent ceases, indicating that the width of the depletion layer becomes thinner than the penetration length of light.

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