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# An Electrochemical Study of the Photosensitivity of Poly-*N*-vinylcarbazole

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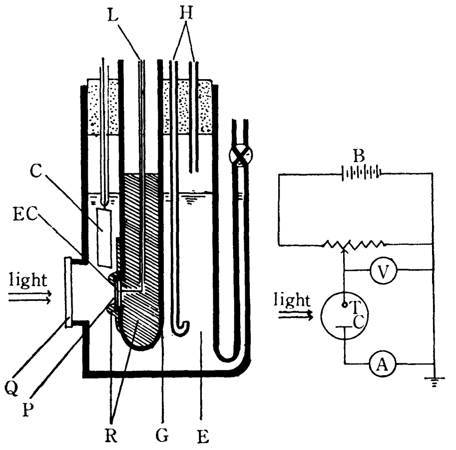
Recently, the photosensitization of ZnO by dyes was studied by means of an electrochemical method, in which dyes were dissolved into a solution and the ZnO crystal was used as a test electrode; it was found that the photosensitization of ZnO by dyes is due to direct electron transfer from excited dyes to ZnO.[1-6] These studies also showed the usefulness of the electrochemical method for the investigation of the photosensitivity of a semiconductor material. In this communication, the application of the electrochemical method to the study of the photosensitivity of poly-*N*-vinylcarbazole (PVCz) will be reported. As is well known, PVCz has a high electronic resistivity, which causes various difficulties in the electrochemical measurements. However, the usefulness of this method will be demonstrated in this paper. The improvement of the photosensitivity of PVCz by the addition of dyes has already been reported[7-9] for a mixed solid system of PVCz and dyes.

## Experimental

The PVCz film was prepared by the method described by Okamote *et al.*,[7] using commercial PVCz (Lubican M 170). Evaporated gold or silver paste was used as the electrical contact. No remarkable difference due to the contact material was found. The assembly of the PVCz electrode is shown in Fig. 1, in which a cell assembly is also shown. The PVCz electrode was dipped in a 2 N $H_2SO_4$ aqueous solution for at least 2 hr before being set in a cell which contained a 0.1 N $H_2SO_4$ aqueous solution. A freshly-prepared electrode was used for each measurement.

The current was measured by means of a pico-ammeter equipped with a current compensator for the residual current. Measurements were made at 25°C by means of the circuit schematically shown in Fig. 1. No reference electrode was used in this study, and the potential differemce between the PVCz electrode and the counter electrode was recorded. As will be described below, the current was so small that the polarization of the counter electrode was almost negligible. In this case, the platinized platinum counter electrode probably acts as an oxygen electrode[10] or as a hydrogen peroxide electrode.[11]



(a) (b)

Fig. 1. Schematic illustration of a cell assembly (a) and a circuit for measurements (b). P: PVCz, EC: electrical contact, R: epoxy resin, G: glass tube, C: counter electrode (platinized platinum), E: electrolyte, L: lead wire, Q: quartz plate, H: nitrogen inlet and outlet, B: dry battery, V: voltmeter (input resistance $10^{11}\,\Omega$), A: pico-ammeter

A 500 W xenon arc lamp was used as the light source. Various color glass filters, different by 50—60 nm in cut-off wavelength, were chosen for the measurements of the spectral sensitization of PVCz by Rhodamine B.

## Result

Figure 2 shows the *I-V* curves of the PVCz electrode in 0.1 N $H_2SO_4$. The photocurrent in this figure was measured under the illumination of a xenon lamp without any filters. It may be observed in this figure that the anodic current was larger than the cathodic current for the same polarization voltage. Figure 3

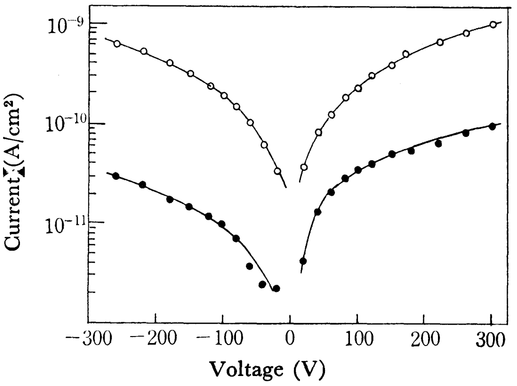


Fig. 2. *I-V* curves of the PVCz in 0.1 N $H_2SO_4$. -●- dark current, -○- photocurrent

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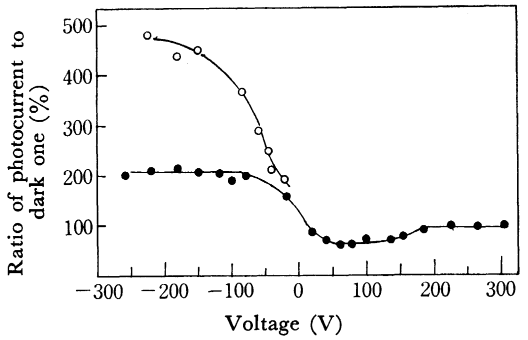

Fig. 3. A ratio of photocurrent to the dark one under illumination of xenon lamp.
-●- PVCz, -○- PVCz+1 mol% TCNE

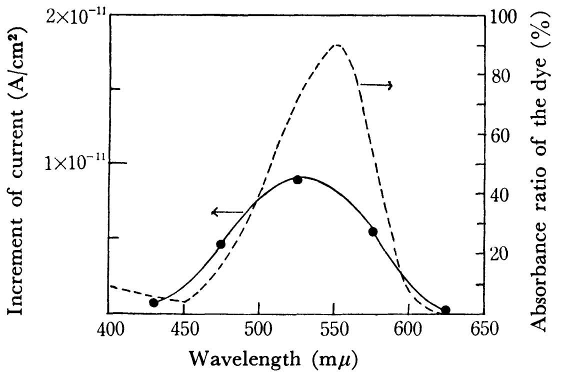

Fig. 4. Spectral sensitization of PVCz by addition of $10^{-5}$ M Rhodamine B to 0.1N $H_2SO_4$.
Solid line: increment of the cathodic current
Dotted line: absorption spectrum of the dye

shows the ratio of the photocurrent to the dark one, which was estimated on the basis of Fig. 2. This figure clearly shows that the ratio was by far larger for the cathodic than for the anodic polarization. The current ratio obtained on the PVCz electrode containing 1 mol% tetracyanoethylene (TCNE) as an electron acceptor[12] is also shown in the figure.

A noticeable spectral sensitization, one which accords with the absorption spectrum of the dye, was observed in the electrolyte containing $10^{-5}$ M Rhodamine B when the electrode was polarized cathodically. Figure 4 shows the increment of the cathodic photocurrent at −250V by the addition of the dye. No increase of the anodic current by the addition of the dye was observed.

## Discussion

When the PVCz electrode was polarized cathodically, the electron energy in the surface region of the electrode becomes lower than that in the bulk of the electrode. Therefore, there must exist an electric field which drifts free electrons from the bulk to the surface and positive holes from the surface to the bulk. In this case, the free electrons, which move from the bulk to the surface and then transfer to a species in the electrolyte, will increase in number upon illumination if the illumination produces the large number of electrons as well as positive holes. On the other hand, if no excited species is produced in the electrolyte by the illumination, the cathodic current due to positive holes will not be influenced by the illumination. Similarly, free holes produced by the illumination will increase the anodic current, while this current will not be increased by photogenerated free electrons if the illumination does not produce any excited species in the electrolyte. Hence, it can be said, from the *I*-*V* curves in the electrolyte without dyes (Fig. 2), that the cathodic current and the anodic current are carried by electrons and holes respectively. The high current gain upon the illumination which was observed on the cathodic polarization is ascribed to the fact that the electrons are the minority carriers.

On the basis of such considerations, the increase of the cathodic current caused by the excited dye indicates that the injection of a positive hole from Rhodamine B into the PVCz electrode occurred, while the injection of an electron from the dye to the electrode probably did not occur.

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