JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 683–692

Photo-electrochemical solar cells with a SnO_2–liquid junction sensitized with highly concentrated dyes

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Received 24 July 1985; final revision 30 October 1985

The sensitization of a SnO_2–liquid junction cell with highly concentrated dyes was investigated. The dyes used were Crystal Violet, Methyl Violet B, Malachite Green, Pararosaniline, and Rhodamine B. Anomalous or positive photovoltages were obtained in the system when $Fe(CN)_6^{3-}$ was added. The performance of the photovoltaic cells showed an open-circuit photovoltage, V_{oc}, of 175 mV, a short-circuit photocurrent, I_{sc}, of 12 μA, and a fill factor of 0.42. The action spectra resembled the absorption spectra of the aggregated dyes. A D–D mechanism is introduced to explain the anomaly of the photovoltage of the SnO_2 electrode sensitized with the dyes. This behaviour is relevant to the practical usage of such photo-electrochemical cells and merits further investigation.

1. Introduction

Photo-cells are important devices in converting solar energy to electricity. Photo-electrochemical cells have advantages over conventional silicon solar cells in that charge separation of photo-excited molecules occurs at the junction boundary which is produced simply by dipping the semiconductors, preferably of the n-type, into certain solutions. The requisite properties of the semiconductors are as follows: (1) that they absorb as much solar light as possible, (2) that they are stable and insoluble at the working condition, (3) that they produce large photovoltage, i.e. have negative flat band potential, and (4) that a large area of material is obtainable at low cost [1].

TiO_2 (3.2 eV), ZnO (3.2 eV), and SnO_2 (3.8 eV) have large band gaps and do not fulfil the first requirement but fulfil the second requirement. Accordingly, dye sensitization has been tried on these substances to expand the absorbable light region. Dye sensitization of semiconductors has been reported by many authors [2–14]. Spitler and Galvin [2] investigated electron transfer from the excited state of xanthene dye to the conduction band of TiO_2 or ZnO single crystal and determined a quantum efficiency of 4.0×10^{-3} for the photo-injection of electrons regardless of the dye concentration at the surface of the crystals.

Concerning the relatively low quantum efficiency of electron injection of Methylene Blue to ZnO single crystals, Yamase *et al.* [3] studied the spectral sensitization of the dye at highly and moderately doped ZnO single crystal electrodes, and obtained the result that the low quantum efficiency was attributable to a number of effective quenching processes such as surface state, fast singlet–triplet transition etc. Moellers and Memming [4] carried out attenuated total reflection (ATR) spectroscopic observations and observed the formation of semioxidized species; they proposed a two-step oxidation of the dyes.

Memming [5] suggested that the quantum efficiency of the photocurrent induced by J-aggregate of cyanine dyes at SnO_2 electrodes was lower than that of monomers. One of the present authors discovered the generation of cathodic photocurrents at SnO_2 electrodes when sensitized with highly concentrated dyes in the presence of dissolved oxygen [6]. Hada *et al.* [7] examined J-aggregates of cyanine dyes on transparent ZnO electrodes for the sensitization of both anodic and cathodic photocurrents. The sensitization was dependent on the kind of dyes employed.

Arden and Fromherz [8] studied the sensitization by cyanine dyes fixed in lipid bilayers on semiconductor electrodes. The electron transfer from the first excited singlet state of the monomer of a cyanine dye occurred at a rate of about 10^{10} s^{-1} but the rate did not depend on the electric field [8].

In this paper we describe an electrochemical solar cell fabricated with a liquid–SnO_2 junction and sensitized by highly concentrated dyes.

2. Experimental details

2.1. *Materials and instruments*

The following triphenylmethane dyes were used for the sensitization experiments: Crystal Violet (Merk), Methyl Violet B (Nakarai Chem.), Pararosaniline (Nakarai Chem.) and Malachite Green (Eastman Kodak), together with a xanthene dye, Rhodamine B (Kanto Chem.). These materials were of guaranteed grade and used without further purification. Solutions of 10^{-6}–10^{-3} mol l^{-1} were prepared by dissolving the dyes in 0.1 mol l^{-1} KCl electrolyte without the addition of buffer substances in order to avoid complexity of the systems. To this was added $Fe(CN)_6^{3-}$ as an acceptor. The dye solutions were aged in a dark storage beaker for more than 2 days before measuring the sensitization.

The NESA glass (SnO_2 transparent films on glass) prepared by thermal oxidation of vacuum evaporated tin films on glass were supplied from the Matsuzaki Vacuum Corp. Its surface resistance was about 1.5×10^2 Ω cm^{-1}, and the donor density was estimated to be about 6.5×10^{19} cm^{-3} from a Mott–Schottky plot assuming the dielectric constant for SnO_2 is 10. Electrical contact to the NESA glass was made using silver butylacetate paste after vacuum evaporation of indium metal on the SnO_2. The electrolytic cell was a 500-ml glass vessel with an SnO_2 (NESA glass) window and a lid equipped with a Luggin capillary, a counter electrode and gas inlet and outlet tubes. Illumination was carried out with a 500-W xenon lamp and wavelengths below 480 nm were cut off by a Y-48 filter (Toshiba Glass Co.). The light intensity was adjusted to 100 mW cm^{-2}.

2.2. *Measurement of photovoltages*

After filling the electrolytic cell with the dye solution, argon gas was bubbled through for about 20 min to expel the dissolved oxygen. The potential of the SnO_2 electrode was measured using an electrometer (Takeda Riken TR-8651) with reference to a saturated calomel electrode (SCE) keeping the platinum counter electrode in open circuit to SnO_2. The SnO_2 electrode was illuminated from the back.

2.3. *Measurement of the photoelectrochemical cell performance*

SnO_2–dye solution–platinum cells were constructed using the above-mentioned dye solutions. The distance between the SnO_2 and platinum was about 5 cm. The photovoltaic currents and photovoltages were measured by means of the electrometer.

2.4. *Amount of dyes adsorbed on SnO_2*

To investigate the relation between the anomalous sensitization and the amount of dye, isothermal adsorption curves were obtained using SnO_2 powder in place of the SnO_2 NESA glass electrode. SnO_2 powder was sieved through 150 and 200 mesh screens and the particle size and shape were determined by electron microscope. SnO_2 powder (1 g) was suspended in 20-ml batches of dye solution of given concentration and kept in the dark at 23° C for 2 days. From the decrease of the optical densities of the dye solutions the amounts of the dyes adsorbed were estimated.

2.5. *Redox reactions of dyes in thin layer cells*

To obtain the changes of absorption spectra of the dye solutions as a function of applied potential, a transparent thin layer cell was employed in the same manner as by Watanabe and Honda [14]. The optically transparent thin layer cell was fabricated by sandwiching a Teflon spacer (0.2 mm thick) between an SnO_2 NESA glass electrode and a Pyrex slide glass. The dye solution was inserted into the space of the cell and the cell was set in the sample chamber of a UV spectrometer together with another empty cell as reference. A potential was applied to the SnO_2 electrode in the sample cell using a potentiostat with SCE as the reference electrode. As soon as the current attained steady state, absorption spectra were measured. For the acetonitrile system, acetonitrile was distilled over P_2O_5 after 1 day of dehydration with molecular sieves and a reference electrode of Ag–0.01 N $AgNO_3$ was used.

3. Results and discussion

3.1. *Photovoltages of SnO_2 electrode sensitized with concentrated dyes*

Fig. 1 shows photovoltages of the SnO_2 with illumination at $\lambda > 480$ nm when sensitized with 10^{-4} mol l^{-1} dyes, along with $Fe(CN)_6^{3-}$. Here, the photovoltage is defined as the potential difference of the SnO_2 electrode between the illuminated condition and in the dark, i.e. E_{ill} to E_{dark}, when measured with reference to a SCE. The potentials of the SnO_2 electrode were about 9 mV versus SCE in the dark.

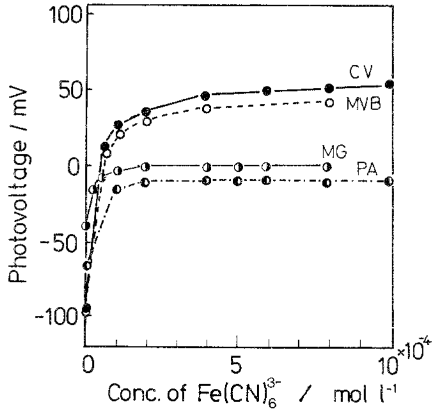

Fig. 1. Relation between photovoltage and concentration of $Fe(CN)_6^{3-}$ at illuminations $\lambda > 480$ nm for SnO_2 electrode sensitized with 10^{-4} mol l^{-1} dyes.

Usually the photovoltages had negative values for dilute dyes — this is normal sensitization or anodic sensitization and is caused by electrons transferring from the photoexcited dyes to the conduction band of the SnO_2 electrode. However, positive values were sometimes obtained when the concentration of the dyes was above 10^{-5} mol l^{-1} in the presence of $Fe(CN)_6^{3-}$. This anomalous behaviour was enhanced with increase of $Fe(CN)_6^{3-}$ concentration although it saturated above a concentration of 10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$. A similar behaviour was observed for dissolved oxygen [6]. It is considered that electron acceptors are necessary for the occurrence of such behaviour so that the dyes can transfer their excited electrons to the electron acceptors, thus changing the SnO_2 electrode to more positive values (namely, cathodic sensitization). The anomalous sensitization of the dyes was dependent on the kind of dye: Crystal Violet and Methyl Violet B showed large tendencies but Pararosaniline and Malachite Green showed small tendencies. It was also affected by the ageing of the dye solutions (Fig. 2).

The history of the SnO_2 electrode in aqueous solution also accounts for the cathodic sensitization: new electrodes sometimes showed a negative photovoltage while used electrodes showed positive values. Bressel and Gerischer [15] explained this in the following way: the surface of SnO_2, which had been prepared by a chemical vapour deposition method, changed to hydroxide in aqueous solutions and electronic levels of hydroxide were formed in the oxo/hydrate layer in the band gap.

3.2. *Performance of the photovoltaic cells*

Fig. 3 shows the photovoltaic performance of the cell SnO_2–dye solution–platinum when sensitized with anomalously behaving Crystal Violet in the presence of 5×10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$. The counter electrode was a platinum plate and light of $\lambda > 480$ nm and 100 mW cm^{-2} was used. A cell with 5×10^{-4} mol l^{-1} Crystal Violet, which was aged in a storage beaker for 3 days after preparation, showed an open-circuit photovoltage, V_{oc} of 90 mV, a short-circuit photovoltaic current, I_{sc}, of 2.6 μA, and fill factor of 0.47. With 10^{-3} mol l^{-1} Crystal Violet,

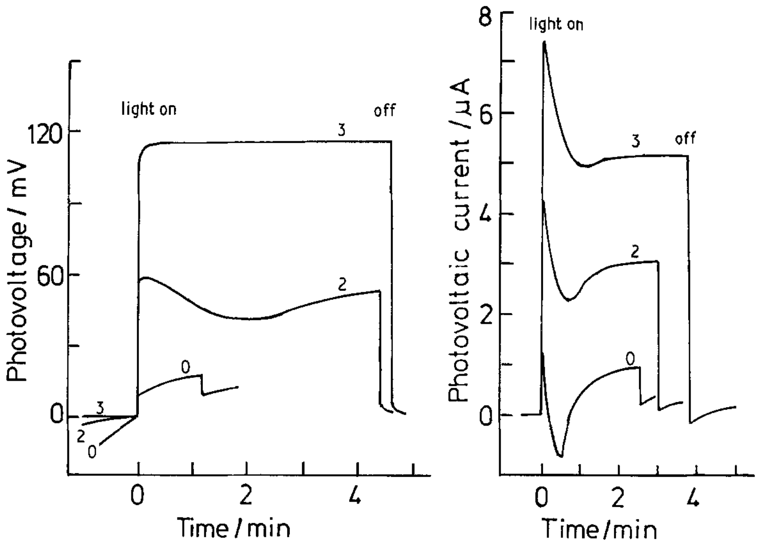

Fig. 2. Time profile of an SnO_2–liquid junction cell sensitized with 10^{-3} mol l^{-1} Crystal Violet in the presence of 5×10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$. Inserted numbers show the ageing time (in days) of the dye solution after preparation.

4 days after preparation, those values were 175 mV, 12 μA, and 0.42, respectively.

Photovoltaic signals from the cells showed fast transient spikes which decreased gradually to reach steady states (Fig. 2). This transient was particularly conspicuous in the short-circuit signals, I_{sc}. The intensity of the transient signals was dependent on the ageing period of the dye solution. Freshly prepared dye solution gave a complicated time profile. The photovoltage of the cell increased linearly with the intensity of the light up to about 10 mW cm^{-2}, but logarithmically in the region of stronger intensity.

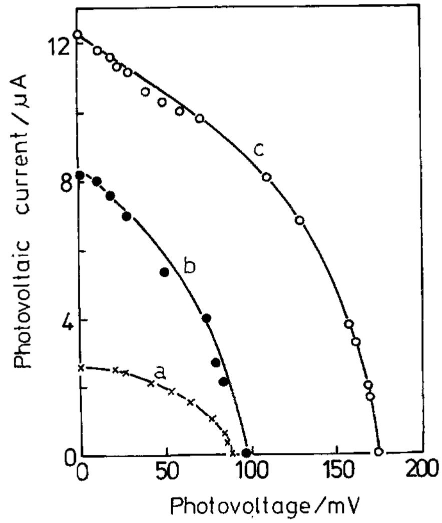

Fig. 3. Performance of an SnO_2–liquid junction cell sensitized with Crystal Violet. In the presence of 5×10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$ with (a) 5×10^{-4} mol l^{-1}; (b, c) 10^{-3} mol l^{-1}. (a, b) Measured 3 days after the preparation; (c) measured 4 days after the preparation. Fill factors for (a) (b) and (c) are 0.47, 0.40 and 0.42, respectively.

3.3. *Photovoltage action spectra of the photovoltaic cells*

Fig. 4 shows the action spectrum of the photovoltaic cell when sensitized with anomalously behaving Crystal Violet. The action spectrum showed a peak of about 540 nm. It resembled the UV–Vis absorption spectra of

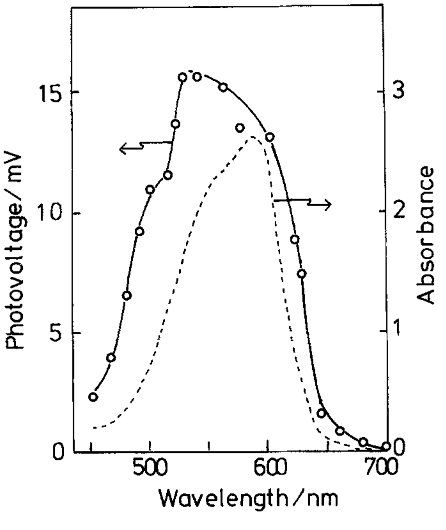

Fig. 4. A photovoltage action spectrum of an SnO_2–liquid junction cell with 10^{-4} mol l^{-1} Crystal Violet in the presence of 5×10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$.

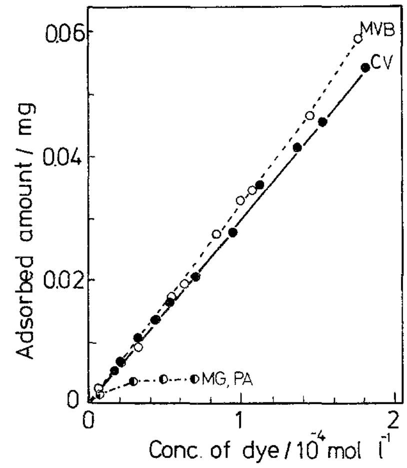

Fig. 5. Isothermal adsorption curves of dyes on SnO_2 powder at 23° C in aqueous solutions.

Crystal Violet dimer and/or the aggregated state [16–23]. Crystal Violet is known to shown two maximum absorption peaks at 540 nm (for dimeric state) and at 585 nm (for monomeric state), and the dye solution used for this experiment (10^{-4} mol l^{-1}) has been proved to be in a mixed state of these two. Therefore, the observed single peak in the action spectrum of photovoltage signifies that the dye is adsorbed on the SnO_2 electrode in at least a bilayered aggregated structure. This has been proved from the isothermal adsorption curves of the dye as shown in Fig. 5.

3.4. *Adsorption of dyes on SnO_2 powder*

The isothermal adsorption curves of the dyes per gram SnO_2 showed that Methyl Violet B and Crystal Violet were adsorbed without saturation in the range of the experiment (Fig. 5).

From SEM observation each SnO_2 particle was about 90 μm in diameter. By assuming the cross-sectional area of the dye and the surface area of the SnO_2, the thickness of the adsorbed dye on the SnO_2 powder was estimated as

$$\begin{aligned} S_{\text{dye}} &= (\text{cross-sectional area of one} \\ &\quad \text{molecule of dye}) \times (\text{number of} \\ &\quad \text{dye molecules necessary to cover} \\ &\quad SnO_2 \text{ particle in monolayer}) \\ &= 0.89 \times 10^7 \, W \text{cm}^2 \qquad (1) \end{aligned}$$

where W is the weight of dye adsorbed in a monolayer. The surface area of 1 g SnO_2 powder was estimated as

$$\begin{aligned} S_{SnO_2} &= (\text{surface area of one} \\ &\quad \text{particle of } SnO_2 \text{ powder}) \\ &\quad \times (\text{number of particles} \\ &\quad \text{in 1 g } SnO_2 \text{ powder}) \\ &= 96.6 \, \text{cm}^2 \qquad (2) \end{aligned}$$

From Equations 1 and 2, W is deduced to be 0.0108 mg. Thus, Methyl Violet B is considered to be adsorbed on the SnO_2 in a multilayer. The same consideration is true of Crystal Violet.

3.5. *Photocurrent induced by dye sensitization with potentiostatic polarization*

Fig. 6 shows the potentiostatic polarization curves of 10^{-4} mol l^{-1} dye solutions. For Crystal Violet solution, which did not contain $Fe(CN)_6^{3-}$, no dark current flowed in the region of -0.2 to $+0.7$ V versus SCE. Dark current was observed above $+0.7$ V versus SCE, suggesting that the dye was oxidized to the $D^{+\cdot}$ cation radical (see Fig. 8). At illuminations of $\lambda > 480$ nm a photocurrent was produced above $+0.2$ V versus SCE. This type of sensitization is normal (or anodic) and arises from the transferring of electrons from the photoexcited dye to the conduction band of the SnO_2 electrode. When the dye solution contained $Fe(CN)_6^{3-}$, photocurrents were not found up to $+0.6$ V versus SCE. Instead, a cathodic photocurrent was produced below $+0.2$ V versus SCE where the reduction of $Fe(CN)_6^{3-}$ took place. The value $+0.2$ V was considered to be the flat band potential of the SnO_2 electrode observed in the previous experiments [6]. The cathodic photocurrent was saturated at a value proportional to the limiting current of $Fe(CN)_6^{3-}$ in the dark.

Similar behaviour was observed in solutions of the other dyes used in this experiment. Table 1 summarizes the values of anodic photocurrents obtained in these systems. The suppression of anodic photocurrent took place easily for the dyes which had a tendency to show positive photovoltages, e.g. it was about 85% for Crystal

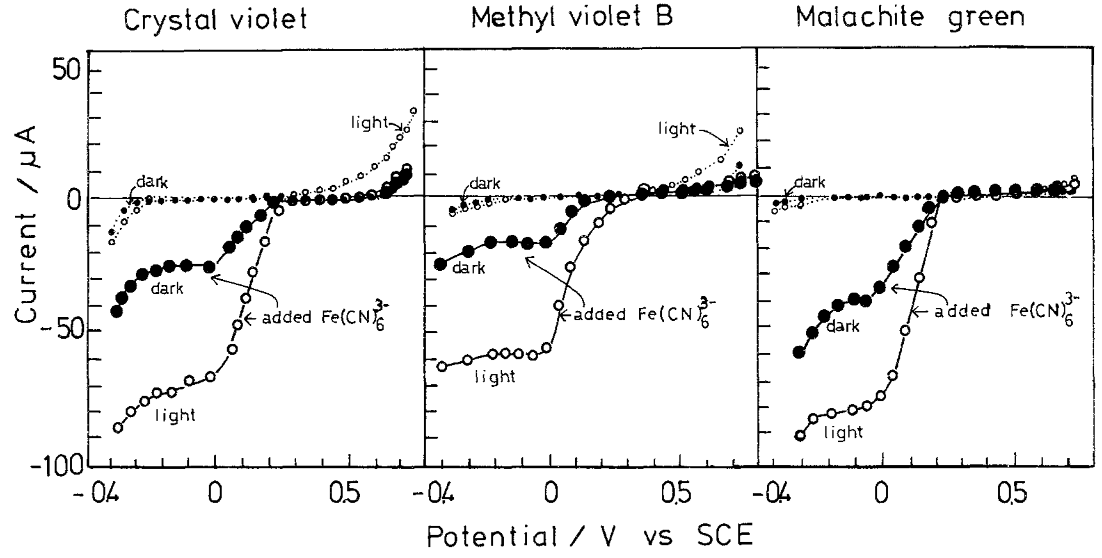

Fig. 6. Photocurrent induced by 10^{-4} mol l^{-1} dyes at potentiostatic polarization. Illuminated at $\lambda > 480$ nm.

Violet solution but 15% for Pararosaniline solution. This fact suggests that the aggregated dyes could transfer their photoexcited electrons either to the conduction band of the SnO_2 electrode or to $Fe(CN)_6^{3-}$ under anodic polarization. The appearance of the cathodic photocurrent was independent of the degree of dye aggregation, since almost the same photocurrent was obtained for each dye.

In a simple $Fe(CN)_6^{3-}$ solution of 5×10^{-4} mol l^{-1} which did not contain any dye a small cathodic photocurrent was observed at a potential below +0.2 V versus SCE with illumination at $\lambda > 480$ nm, but it was negligible compared with the photocurrent obtained in the solutions with the dyes.

3.6. *Redox potentials of the dyes*

To examine the anomalous sensitization the redox potentials of the dyes were determined on an SnO_2 electrode in acetonitrile solutions containing 0.2 mol l^{-1} $NaClO_4$ by cyclic voltammetry. As shown in Fig. 7, oxidiation and reduction current peaks for Crystal Violet were found at 0.79 and 0.73 V versus Ag–0.01 N $AgNO_3$, respectively. Thus, the equilibrium potential between Crystal Violet and its oxidized species $D^{+\cdot}$ (see Fig. 8) was deduced to be 0.76 V versus Ag–0.01 N $AgNO_3$, i.e. 0.79 V versus SCE. Since the excitation energy of Crystal Violet is estimated as 2.10 eV from the maximum absorption wavelength (590 nm), the equilibrium potential between the excited state and the oxidized species $D^{+\cdot}$ of Crystal Violet was deduced to be − 1.31 V versus SCE. In this way, redox potentials of other dyes used in this experiment were determined (Table 2). Pararosaniline could not be oxidized in this experiment (see Fig. 8), so the current peaks due to the

Table 1. Anodic photocurrent and effect of $Fe(CN)_6^{3-}$ *at the illumination of* $\lambda > 480$ *nm light*

	Anodic photocurrent (at E = 0.6 V versus SCE)		
	10^{-4} mol l^{-1} dye (1) (μA)	*10^{-4} mol l^{-1} dye and 5×10^{-4} mol l^{-1} $Fe(CN)_6^{3-}$ (2) (μA)*	(2)/(1)
CV	11.9	1.8	0.15
MVB	10.7	2.6	0.24
PA	1.2	1.02	0.85
RhB	2.2	0.86	0.39

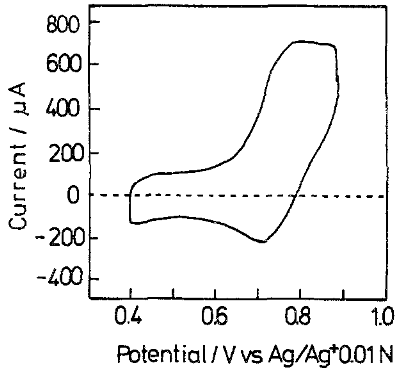

Fig. 7. Cyclic voltammogram of 10^{-3} mol l^{-1} (dissolved in 0.2 mol l^{-1} $NaClO_4$ acetonitrile) on an SnO_2 electrode. Sweep rate: 100 V s^{-1}.

formation of cation radicals (anodic current) and the reduction of the radical (cathodic current) were not observed. Thus, the excited level and the redox potential of Pararosaniline could not be determined.

Since Rhodamine B is a dye of higher excited state, it is considered that electron transfer from the excited dye should be brought about more easily for Rhodamine B. Furthermore, the transfer should be possible for both directions, i.e. to the SnO_2 electrode and to the $Fe(CN)_6^{3-}$ in the solution, the latter resulting in cathodic or anomalous sensitization of the SnO_2 electrode. Since Malachite Green is a dye of higher ground state, it should transfer the electron of the ground state to $Fe(CN)_6^{3-}$ by thermal activation more easily. In fact, the anomalous sensitization was brought about more easily by Crystal Violet and Methyl Violet B. Therefore the difference of energy levels of the dyes cannot be a good explanation of the anomalous sensitization. It should be noticed that the dyes were entirely in the monomeric state in acetonitrile solutions although high concentrations of the dyes were employed (see Fig. 8). In aqueous solution, an aggregated state was favoured at high concentration, but the cyclic voltammogram did not show current peaks corresponding to the reduction of their cation radicals $D_{ag}^{+\cdot}$ which had been produced by anodic polarization. This is probably due to the disappearance of cation radicals in a fast reaction with solvent [24] or H_2O. Redox potentials could not be obtained for aggregated dyes in the aqueous solutions.

3.7. *Absorption spectra of the dyes in a thin layer cell*

The absorption spectra of the dyes were measured in a thin layer cell while applying potentials. Fig. 8 shows the results for the dyes in acetonitrile solutions without $Fe(CN)_6^{3-}$. With anodic polarization the absorption peaks of the dyes began to decrease and, at the same time, began to show new peaks at about +0.70, +0.72, +0.70 and +0.80 V versus Ag–0.01 N $AgNO_3$ for Crystal Violet, Methyl Violet B, Malachite Green, and Rhodamine B, respectively. Pararosaniline, however, never changed the absorption spectrum with the anodic polarization in this experiment. The new peaks were found at 624, 614, 528 and 496 nm for Crystal Violet, Methyl Violet B, Malachite Green and Rhodamine B, respectively. When the logarithm of the ratios of the intensities of the new and original peaks, $\log(D_{new}/D)$, was plotted against potential, E, essentially straight lines were obtained of which the slopes were about 60–68 mV, almost equal to $2.303\,RT/F$. Therefore, these dyes were considered to make one electron transfer and

Table 2. Determined energy levels of dyes

	CV	*MVB*	*MG*	*RhB*
Oxidation peak, U_A (V)	0.785	0.800	0.780	0.890
Reduction peak, U_C (V)	0.725	0.735	0.725	0.835
$\Delta E = U_A - U_C$ (V)	0.060	0.065	0.055	0.055
$E(D/D^{+\cdot})$ in AN (V)	0.755	0.768	0.753	0.863
$E(D/D^{+\cdot})$ in H_2O (V)	0.787	0.800	0.785	0.895
Absorption peak (nm)	590	585	618	553
Excitation energy (eV)	2.102	2.120	2.006	2.242
$E(D^*/D^{+\cdot})$ in H_2O (V)	−1.315	−1.320	−1.221	−1.347

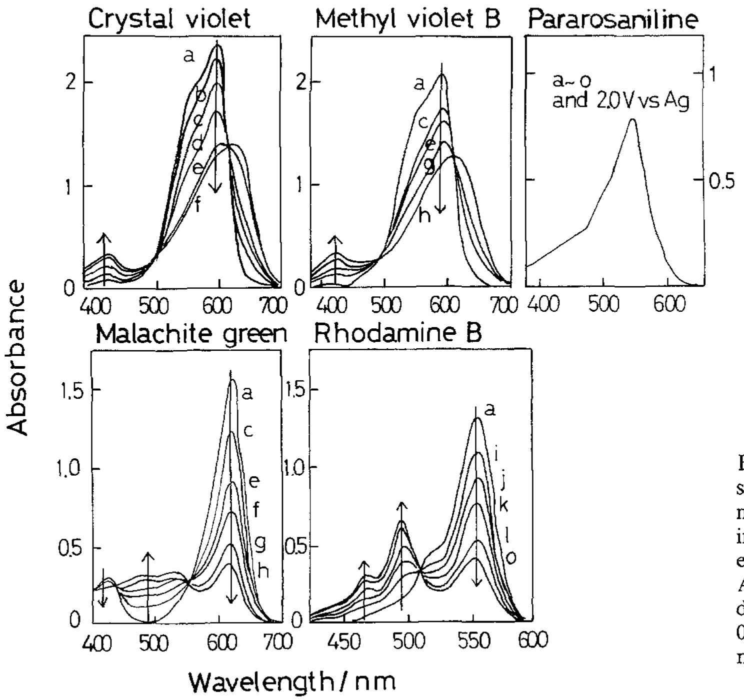

Fig. 8. Absorption spectra of dye (dissolved in 0.2 mol l^{-1} NaClO$_4$ acetonitrile) measured in a thin layer cell. Labels a–o indicate applied potentials on the SnO$_2$ electrode with reference to Ag–0.01 N AgNO$_3$: a, not applied; b, 0.070; c, 0.725; d, 0.750; e, 0.775; f, 0.800; g, 0.825; h, 0.850; j, 0.900; k, 0.925; l, 0.950; m, 0.975; n, 1.000; o, 1.025 V.

become cation radicals at the anodic polarization.

In aqueous solutions, however, these new peaks did not appear (see Fig. 9), presumably because the cation radicals reacted quickly with the solvent [24] or H$_2$O. With cathodic polarization the absorption spectra of the dyes, except for Rhodamine B, changes as shown in the lower part of Fig. 9.

4. Conclusions

Positive photovoltages were generated at an SnO$_2$ NESA electrode when it was sensitized with highly concentrated dyes in the presence of Fe(CN)$_6^{3-}$. This sensitization is anomalous since electrons transfer from the electrode to the photoexcited dyes while they move from photoexcited dyes to the electrode in an ordinal sensitization. The anomaly depended on the kind of dyes and increased with the ageing of the dye solutions. With the sensitization, action spectra of photovoltages and photovoltaic currents similar and peculiar to the absorption spectra of aggregated dyes were obtained.

It has been shown by Koizumi and co-workers [25, 26] that for some dyes the triplet-state dye reacts with the ground-state dye to produce a half-oxidized dye and a half-reduced dye (D–D mechanism).

$$^3D^* + D \longrightarrow D^{+\cdot} + D^{-\cdot} \qquad (3)$$

The D–D mechanism is operative in aerated solution when the dye concentration is high. But the D–O mechanism operates at lower concentrations of the dye. In this condition, judging from the small quantum yield for the oxidative bleaching of the dye, most of the D$^+$ . . . O$_2^-$ complex seems to revert to the original dye and oxygen. The switch-over from the D–O to the D–D mechanism occurs at higher dye concentrations for higher oxygen concentrations. The intermediate D$^{+\cdot}$ . . . $D^{-\cdot}$ in the D–D mechanism reacts with oxygen (see Equation 4) and the rate of the reaction increases with the oxygen concentration.

$$D^{+\cdot} \ldots D^{-\cdot} + O_2 \longrightarrow D^{+\cdot} + D + O_2 \qquad (4)$$

The photochemical reaction of dye with Fe(CN)$_6^{3-}$ was investigated by Kashe and Lindquist [27] using flash-photolysis on 0.5 μmol l^{-1} eosin, and the following reaction scheme was presented for the results:

$$^3D^* + Fe(CN)_6^{3-} \longrightarrow D + Fe(CN)_6^{3-} \qquad (5)$$

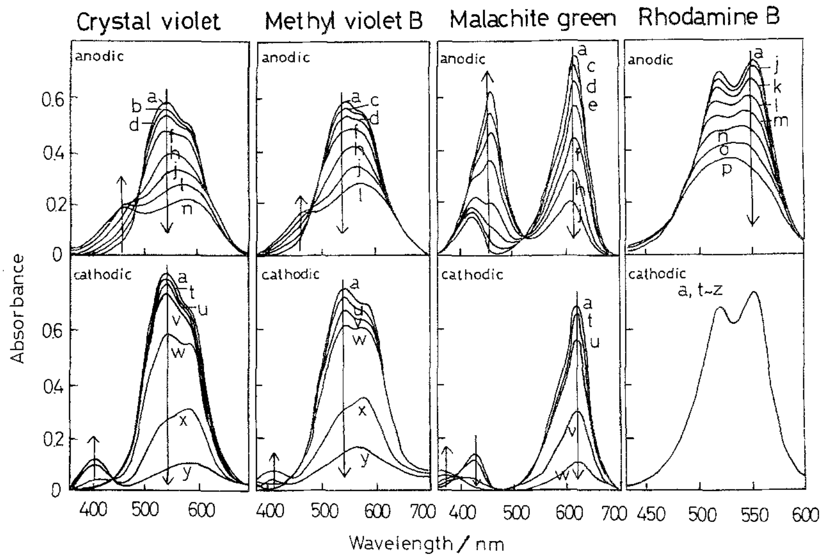

Fig. 9. Absorption spectra of dye (dissolved in 0.1 mol l^{-1} aqueous KCl) measured in a thin layer cell. Labels a–z indicate applied potentials on the SnO_2 electrode in reference to SCE: a, not applied; b, 0.700; c, 0.725; d, 0.750; e, 0.775; f, 0.800; g, 0.825; h, 0.850; i, 0.875; j, 0.900; k, 0.925; l, 0.950; m, 0.975; n, 1.000; o, 1.025; p, 1.050; q, 1.075; r, 1.100; s, 1.125; t, −0.3; u, −0.4; v, −0.5; w, −0.6; x, −0.7; y, −0.8; z, −0.9 V.

$$^3D^* + Fe(CN)_6^{3-} \longrightarrow D^{+\cdot} + Fe(CN)_6^{4-} \quad (6)$$

$$D^{+\cdot} + Fe(CN)_6^{3-} \longrightarrow D + Fe(CN)_6^{3-} \quad (7)$$

The rate constants were 1.0×10^8 and 1.5×10^8 $mol^{-1}\,s^{-1}$ for Equations 5 and 6, respectively. The semioxidized eosin was formed in high yield, but it rapidly reverted to the original dye according to Equation 7.

Memming and Kuersten [28] have reported for photochemical and electrochemical reactions of excited dyes at metal electrodes that with 10^{-4} mol l^{-1} dye solutions free from any reducing agent but saturated with oxygen, cathodic photocurrents were observed in potential ranges between 0 and −0.5 V with metal electrodes at pH = 6. Photocurrents were also found with other oxidizing agents. From these results it is considered that an excited dye is oxidized with oxygen to become its semioxidized form according to the reaction,

$$D + h\nu \longrightarrow D^* \quad (8)$$

$$D^* \longrightarrow {}^3D^* \quad (9)$$

$$^3D^* + \tfrac{1}{2}O_2 + H_2O \longrightarrow D^{+\cdot} + 2OH^- \quad (10)$$

$$D^{+\cdot} + e\ (\text{electrode}) \longrightarrow D \quad (11)$$

thus explaining the generation of a cathodic photocurent at the metal electrode.

The electrode we used was an n-type semiconductive SnO_2, but it behaved like a metal electrode in regard to the generation of cathodic photocurrent and positive photovoltage. This behaviour is attributable to the tunnelling of electrons from the conduction band of the SnO_2 electrode to the dye adsorbed on the electrode across the energy barrier at the SnO_2–liquid junction when the dye has been semioxidized by D–D to $D^{+\cdot}$ . . . D. The tunnelling mechanism is reasonable for the junction barrier because the SnO_2 possesses a high concentration of carriers (3×10^{19}). The fact that the anomalous behaviour occurred easily in used SnO_2 suggests that the surface of the electrode is changed partly to hydroxide by hydrolysis as pointed out by Bressel and Gerischer [15].

Cathodic photocurrents induced by dye sensitization have been observed for both p- and n-type GaP [28]. It is considered that electron transfer takes place from the valence band of n-type GaP to the empty ground state of the dye since GaP has such a high band level as to interact with the ground level of the photo-excited dye [29]. However, SnO_2 does not have such a high band level nor such a moderate band gap as GaP.

The aggregated dyes which are adsorbed on the SnO_2 electrode are considered to become ion pairs $D^{+\cdot} \ldots D^{-\cdot}$ as a result of photoexcitation. When the solution contains electron acceptors such as oxygen or $Fe(CN)_6^{3-}$, the ion pair $D^{+\cdot} \ldots D^{-\cdot}$ reacts with the electron acceptor to become $D^{+\cdot} \ldots D$. $D^{+\cdot} \ldots D$ extracts electrons from the SnO_2 electrode, resulting in the generation of positive photovoltage. The D–D mechanism is useful in explaining the anomalous photovoltages produced by electrodes sensitized with dyes. The behaviour is worthy of further investigation with a view to the practical usage of such photoelectrochemical cells.

Acknowledgements

The authors are indebted to Emeritus Professor S. Tajima and Professor M. Hida of Tokyo Metropolitan University for valuable discussions.

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