

# A dye/polymer based solid state thin film photoelectrochemical cell used for light detection

Sisir Kumar Dey<sup>a</sup>, N.B. Manik<sup>a,\*</sup>, S. Bhattacharya<sup>b</sup>, A.N. Basu<sup>a</sup>

<sup>a</sup>Condensed Matter Physics Research Centre, Department of Physics, Jadavpur University, Calcutta 700032, West Bengal, India

<sup>b</sup>Department of Chemistry, Jadavpur University, Calcutta 700032, West Bengal, India

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## Abstract

In the present investigation solid state polymer photoelectrochemical (PEC) cells have been fabricated for light detection using thin film of blends of optically active Safranin-T dye dispersed in polyvinyl alcohol (PVA) used as an inert polymer matrix and polyethylene oxide (PEO) complexed with ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) ion salt as a solid electrolyte with ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers. A thin film ( $\sim 200$  nm) of this blend is sandwiched between two transparent indium tin oxide (ITO) coated glass plates which act as the two contact electrodes. Upon application of an external bias voltage on the device the photo response is observed while illuminating the device from a tungsten lamp. The measured photosensitivity is about  $0.20 \mu\text{A mW}^{-1} \text{cm}^2$  at a bias voltage of 3.5 V and at an incident intensity of about  $40 \text{ mW cm}^{-2}$ . It is observed that the sensitivity depends on the bias voltage and the nature of this dependence is studied. From the observation on the growth and the decay of the photocurrent at different bias voltages the photosensitivity versus the bias voltage is evaluated. The characteristic feature that emerges from the present study is that the device can be used as a large area photodetector with a somewhat slower speed of response. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Organic photodetector; Solid state photoelectrochemical cell; Plasticizers; Ionic conductivity

## 1. Introduction

Recently, a lot of work has been done on all solid state electrochemical cells using different organic and polymer based photonic and electronic devices such as organic light emitting diodes (OLED) [1,2], light emitting electrochemical cells (LEC) [3–12], solar cells [13,14], transistors [15], electrochromic windows, sensors [16–21] etc. The materials used in these devices have advantages of relatively excellent film forming properties [22], facile colour tunability and adequate mechanical properties [23]. In addition these may be fabricated over a large area on flexible substrate from its solution by simple processing techniques, such as sol–gel, spin-coating, solvent casting, sublimation, dip coating etc. All these devices are basically a thin film ( $\sim 200$  nm) of different active materials like conjugate polymer, organic molecules, liquid crystal along with a solid electrolyte complexed with different ion salt sandwiched by two electrodes. Upon application of external bias on the devices the positive ions are accumulated near the cathode and the negative ones near the anode and a depletion layer is formed

inside the active layer due to the redistribution of charges. It is reported that these solid state electrolytes when biased the polymer is p-doped on the anode side and n-doped on the cathode side and a dynamic reversible p–n junction is formed between the p-doped and n-doped regions [24,25]. The different theoretical models have also been developed [26,27] to estimate the current voltage characteristics in this structure which may be used to understand the limitations of the device performance. The speed is limited on the low ionic mobility of the ion salt. Recently, it has been reported that by using the carrier freeze out technique [9,10] the ionic mobility will freeze out and using different plasticizers with the ionic salt the ionic mobility can also be increased [11].

However, though a number of reports are now available on photoelectrochemical (PEC) solar cell no such works are available on PEC based photodetector. In general, in a photodetector the different processes such as generation of charge carriers due to absorption of light by an optical active material, separation of charge carriers by an applied external field and migration or transport of charges to generate the photocurrent take place. In this work we describe a PEC cell which has been fabricated for optical detection using thin film of blends of organic dye Safranin-T (dispersed in transparent polyvinyl alcohol used as an inert

\* Corresponding author. Tel.: +91-033-472-5868.

E-mail address: nabin@juphys.ernet.in (N.B. Manik).

polymer matrix) as optical active material and polyethylene oxide (PEO) complexed with ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) ion salt as solid electrolyte with ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers. The cell consists of this blend in a thin film as an active material and two transparent indium tin oxide (ITO) coated glass plates as the contact electrodes. It is expected that the salt ion of  $\text{NH}_4\text{ClO}_4$  mixed with PEO acts as the solid electrolyte and provides the counter ions and the ionic conductivity necessary for the doping. Addition of plasticizers EC and PC makes the complexed mixture viscous which helps easy fabrication of the film and also enhances the carrier mobility. The device has a typical sensitivity of the order of  $0.20 \mu\text{A mW}^{-1} \text{cm}^2$  at a bias voltage of 3.5 V and at an incident intensity of about  $40 \text{mW cm}^{-2}$ . The sensitivity largely depends on the bias voltage.

## 2. Sample and cell preparation

Safranine-T (E. Merck, Germany) dye structure shown in Fig. 1 was recrystallised twice from ethanol–water mixture and mixed with PVA (S.D. Fine Chem. Ltd., Boisar; M.W. 125000) used as a transparent inert binder. In a cleaned test tube 5 g. of PVA was mixed with 10 cc of double distilled water, warmed gently and stirred to make a transparent viscous solution of PVA. One milligram of Safranine-T is mixed with this solution. PVA was used here as an inert transparent binder to form the stable film of the dye.

In a separate beaker cleaned by regular processes a solid electrolyte was prepared by mixing PEO (BDH, England; M.W. 600000),  $\text{NH}_4\text{ClO}_4$  (Fluka, 99.5% pure), EC (Fluka, 99.5% pure) and PC (Fluka, 99.5% pure). The complex of PEO,  $\text{NH}_4\text{ClO}_4$ , EC, PC (30.60%, 3.60%, 19.60% and 46.20% by weight) were mixed, stirred and heated around a temperature  $80^\circ\text{C}$  for 5 h. This gel-like solid electrolyte is mixed with the previously prepared dye–PVA solution to form the blend. This blend is heated about a temperature  $80^\circ\text{C}$  and stirred properly to mix them well for about 1 h.

The viscous gel-like solid solution is sandwiched between two transparent ITO coated glasses. The glass plates were cleaned in chloroform solution and dried under vacuum about 5 h before use. The uniform film thickness is controlled by placing two teflon spacers of thickness about 200 nm near the edges of the ITO coated glass plate and two

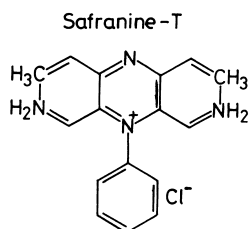


Fig. 1. Structure of the Safranine-T dye.

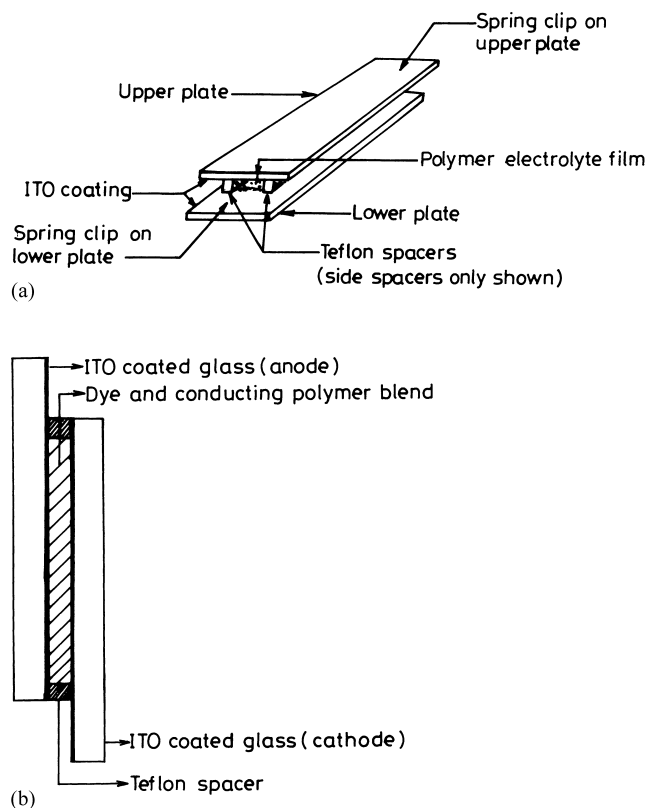


Fig. 2. (a) Schematic structure of PEC; (b) Schematic cross-sectional view of PEC.

spring clips were fixed at a moderate pressure at the ends of the electrodes as shown in Fig. 2 (a) and (b). The two electrical leads are taken out from the two ends of the ITO coated glass. The complete cell is vacuum dried for about 12 h at around  $80^\circ\text{C}$  before the final measurement.

## 3. Dark $I$ – $V$ characteristics

For the dark  $I$ – $V$  characteristics the film is biased with a dc voltage source with a series resistance of 47 K. The current flowing through the device is estimated by measuring the voltage across this sensing resistance. By varying the dc bias the steady voltage across the resistance is measured by a Philips  $4\frac{1}{2}$  digit multimeter. Dividing the measured voltage by the value of this sensing resistance the current flowing through the device is calculated. The value of this current with the dc bias is plotted and is shown in Fig. 3. It is observed that the current takes a lot of time (about 20 min) to reach the steady value after application of each bias voltage. From this curve it is seen that the device turns on at a bias voltage of approximately 1.2 V which seems to be related to the band gap of the dye. The  $I$ – $V$  characteristics are nearly symmetric about the origin for both forward and reverse bias. The  $I$ – $V$  characteristic by changing the polarity of the dc bias is not shown in this figure. The steady state dark  $I$ – $V$  characteristics may be qualitatively explained from the

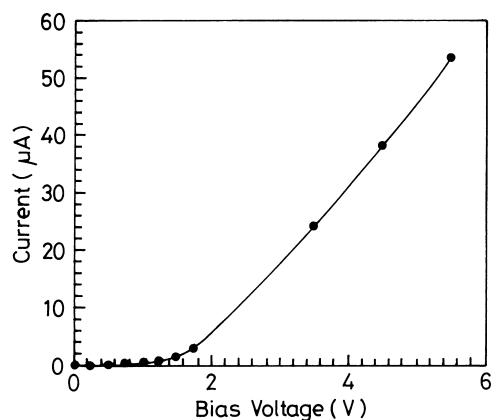


Fig. 3. Dark  $I$ - $V$  characteristics of the device.

theoretical model developed by Smith et al. [26] considering the contribution of different charge carriers i.e. electron, holes and the cations and anions of the ion salt.

The  $\ln I$ - $\ln V$  plot shown in Fig. 4 shows a transition point at a bias voltage around 1.2 V which seems to indicate a change in the conduction mechanism of this device. To explain the change of the conduction mechanism at this voltage the transport of the charge carrier, its trapping and recombination are being studied carefully and will be reported elsewhere.

#### 4. Growth of the photocurrent

The cell is biased with a dc source making any one ITO as anode and with a series resistance of about 47 K as before. Now the light from a tungsten lamp of 200 W is allowed to incident on it. The distance of the lamp from the sample is so adjusted that an intensity of about  $40 \text{ mW cm}^{-2}$  is incident on the device of surface area  $\sim 0.64 \text{ cm}^2$ . The intensity is measured by a calibrated lux meter (Kyoritsu Electrical Instruments Works Ltd. Tokyo, model 5200 with Selenium detector). It is observed that, due to the incident radiation,

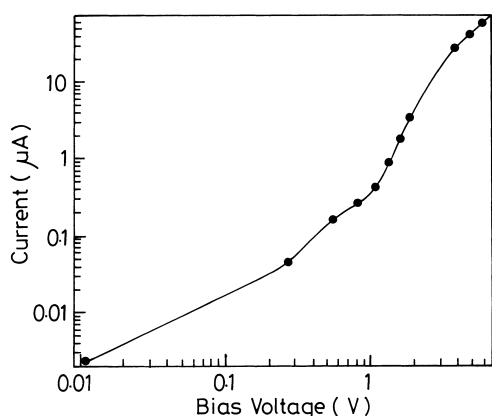


Fig. 4.  $\ln I$ - $\ln V$  plot of dark  $I$ - $V$  characteristics.

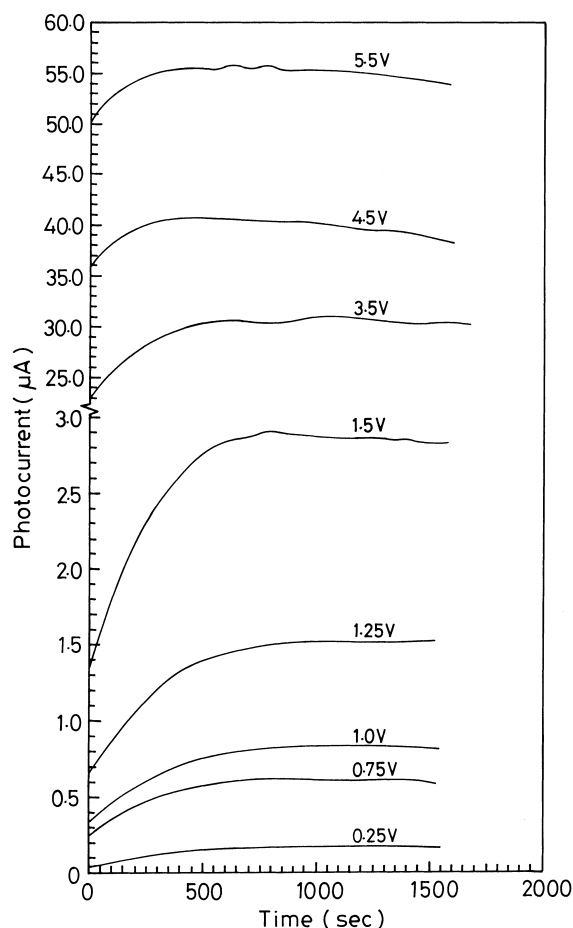


Fig. 5. Optical response of the device for a fixed illumination at different bias voltage.

the voltage across the sensing resistance is increased and is recorded with respect to time. The measurement is repeated for different bias voltages. By dividing the measured photovoltage with the value of the sensing resistance the photocurrent is calculated. This photocurrent for different bias voltages are plotted with time and are shown in Fig. 5. After a certain time the photocurrent is saturated though the saturation value depends on the bias voltage. The measurement is done for a number of times and reproducibility is observed.

#### 5. Sensitivity

From the above curve (Fig. 5) it is observed that due to the incident of radiation intensity  $40 \text{ mW cm}^{-2}$ , the photocurrent changes from an initial value to a final steady one. We define the typical sensitivity as the difference between the dark current and the maximum photocurrent divided by the value of incident illumination (which is  $40 \text{ mW cm}^{-2}$  for the present case) for different bias voltages. And this sensitivity versus voltage has been plotted in Fig. 6. It is interesting to note that the sensitivity initially increases with the bias

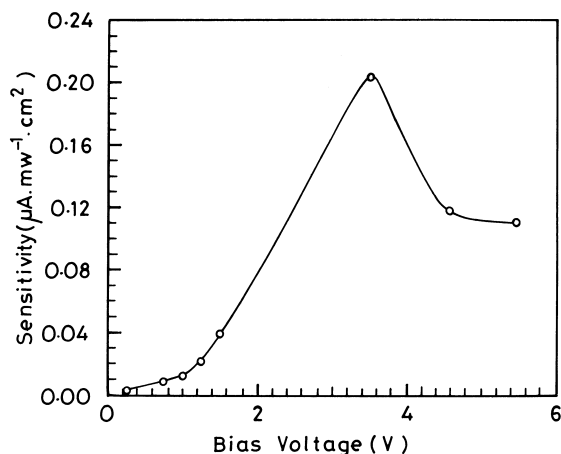


Fig. 6. Sensitivity of the device at different bias voltage.

voltage and reaches a maximum and then decreases with further increase of voltage.

Upon application of bias voltage the cations and the anions of the salt accumulate near the cathode and anode side, respectively, producing a p–n like junction and the internal field originating from this separation of the ion charges helps migration of photo carriers. That the sensitivity increases with the bias voltage up to a certain value for a given intensity of light is due to the fact that the internal field produced by the salt ion accumulation increases with bias voltage. Ionic motion in the polymer blend plays a key role in the electrochemical doping and the formation of the p–n like junction. After the junction is formed, however, the ionic mobility is undesirable [10]. Degradation of the polymer can occur by over oxidation or reduction when the applied bias voltage crosses a certain value. This may be a possible reason for lowering of sensitivity after a certain bias voltage.

## 6. Decay of the photocurrent

After attaining the saturation value of the photovoltage the light is switched off and it is observed that the reading of the multimeter begins to fall. The voltage drop with time is recorded for different bias voltages. Dividing the measured photovoltage by the value of the sensing resistance the photocurrent is calculated as before. This current is plotted with time and is shown in a separate figure, Fig. 7 for different bias voltages. It is observed that the initial photocurrent is restored after a few minutes. The relaxation time being large (order of minutes), it is expected that the relaxation is not electronic in nature. This slow decay is a limitation to use the device for high speed operation.

Though the details of this slow rate of decay is not clear at present it is expected that slow diffusion of ions is largely responsible for this effect. During the decay the salt ion diffuses back into the electrolyte restoring the uniform ionic charge throughout the polymer layer [4]. In addition to this

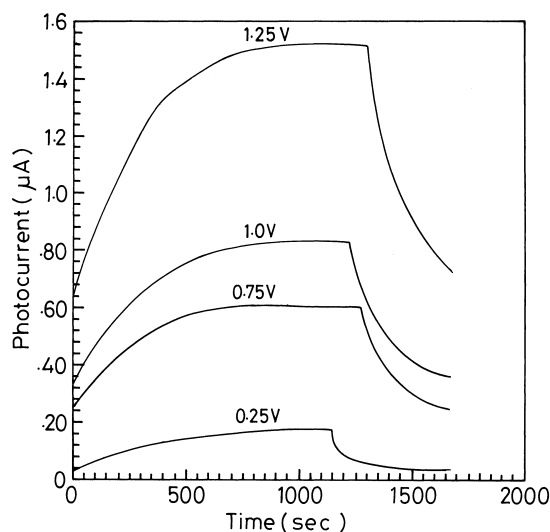


Fig. 7. Optical response (growth and decay) of the device at different bias voltage.

slow diffusion of ions it is expected that some charge trapping phenomena may also occurs.

## 7. Discussion

In this device the dye, Safranin-T is used as an optical sensitive material. The photochemistry of the dye has contributed to the understanding of the mechanism of electron transfer reaction in PEC devices. In general, a photodetector follows the different steps like generation of charge carriers due to absorption of light, separation, migration and transport of these charges. In the present structure the dye is used for generation of charge carrier due to the absorption of optical radiation. The Safranin-T dye being a cationic dye (the structure is shown in Fig. 1) leaves an excess hole (h<sup>+</sup>) due to the absorption of radiation. These charges are separated by the internal field produced by the redistribution of the salt ions after application of the bias voltage.

## 8. Conclusion

Here in this article we report the photoconductivity study in thin film of Saphranine-T dye and polymer complex in a qualitative way. All these effects appear to be interesting and also require further quantitative explanation. Some attempts are being made in this direction. The most important aspect is to correlate the structure-property relation of the material. For this purpose the experiments need to be done by using different materials. Presently, the subject of some controversy, the mechanism for charge carrier generation in organic thin film photovoltaic devices is believed to be due to creation of bound electron–hole pairs, excitons, by absorption of light in the active parts of the devices. Charge

generations occur as a result of dissociation of the excitons by interaction of the excitons with interfaces, impurities, defect, or with high electrical fields.

The device has a low sensitivity in the present form. The use of two transparent electrodes make the device highly transparent. It may be presumed that if one uses one electrode with a reflecting coating instead of a transparent one so that the incident radiation is confined inside the device due to back reflection from the reflecting surface and thereby increases the efficiency. In future we intend to design an experiment in this direction.

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