Study on Photoconductivity of Dye-Polymer-Based Solid-State Thin Film

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Abstract

In this article, we describe a solid-state photoelectrochemical cell for light detection. Safranine-T dye mixed with polyvinyl alcohol (PVA) solution was deposited on a conducting and transparent indium-tin-oxide (ITO)-coated glass that was used as one electrode and another ITO-coated glass as the counterelectrode. A solid polymeric electrolyte consisting of polyethylene oxide-ammonium perchlorate-ethylene carbonate and propylene carbonate with suitable weight ratio was prepared and sandwiched between these two ITO-coated glass electrodes, which were separated by a Teflon spacer about 50 μm thick. The cell was biased with a direct current source to make the dye and PVA-coated ITO as the anode and the other ITO as the cathode. On illumination by a tungsten lamp, from the cathode side, the change of photocurrent was measured. The dark current-voltage characteristics and the growth and decay of the photocurrent for steady and pulsed illumination were studied.

Index Entries: Organic photodetector; solid-state photoelectrochemical cell; photoconductivity.

Introduction

Solid-state electrochemical cells of different organic and polymeric materials are important to development of different photonic and electronic devices such as organic LEDs *(1–7)*, solar cells *(8,9)*, transistors *(10)*, electrochromic windows, and sensors *(11–14)*. Polymeric and organic materials are attractive because of excellent film-forming properties *(15)*, facile color tunability, and adequate mechanical properties *(16)*. All these devices are basically thin films of different organic materials along with a solid electrolyte complexed with ion salt sandwiched between two electrodes. On application of external bias on the device, the positive ions of the solid electrolyte are accumulated near the cathode and negative ions near

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the anode, forming a depletion layer inside the cell owing to the redistribution of charges. It has been reported that when a solid-state, light emitting electrochemical cell is biased, the polymer is p-doped near the anode side and n-doped near the cathode side, and a dynamic reversible junction is formed inside the bulk of the device *(17,18)*. However, the speed of operation of all these solid-state electrochemical cells is poor owing to the lower ionic mobility of the salt. Recently it has been reported that by using a carrier freeze-out technique *(6)* and using plasticizers with the ionic salt, the ion conductivity can be increased *(7)*.

Although a number of reports are available on the emission of light on these solid-state electrolytes *(3–7)*, few reports are available for photo detection. Therefore, in the present study we describe an all solid-state electrochemical cell that was used for optical detection. Thin film of Safranine-T dye dispersed in an inert transparent binder polyvinyl alcohol (PVA) was used as the optically active material. Polyethylene oxide (PEO) complexed with ammonium perchlorate (NH_4ClO_4) ion salt was used as the solid electrolyte with ethylene carbonate and propylene carbonate as plasticizers to enhance ion conductivity.

Materials and Methods

Sample and Cell Preparation

The structure of the Safranine-T (E. Merck, Germany) dye, shown in Fig. 1, was recrystalized twice from an ethanol-water mixture and mixed with PVA (mol wt = 125,000; S. D. Fine Chem. Ltd., Boisar) used as a transparent inert binder to form a gel-like solution. A thin layer (about 200 nm) of this solution was formed on a cleaned indium-tin-oxide (ITO)-coated glass (FL9496; Balzers) by spin-coating method at a motor speed of 1500 rpm. The deposited film was then subjected to thermal treatment under vacuum for about 2 h at 60°C to release the excess free water. In a 25-cc beaker, PEO (mol wt = 600,000; BDH, England) was complexed with NH_4ClO_4 (99.5% pure; Fluka) ion salt as solid electrolyte with ethylene carbonate (99.5% pure; Fluka) and propylene carbonate (99.5% pure; Fluka) as plasticizers to enhance the ion conductivity. The complex of PEO-NH_4ClO_4 ethylene carbonate-propylene carbonate (30.60, 3.60, 19.60, and 46.20%, respectively [w/w]) were mixed, stirred, and warmed gently for about 2 h at 60°C to form the solid electrolyte. The viscous gel-like solid solution of this electrolyte was sandwiched between two ITO-coated glass plates one of which contained previously deposited dye and PVA layer. The uniform thickness was controlled by using two Teflon spacers about 50 µm thick at the two ends of the electrodes, and the electrodes were held together by two spring clips as shown in Fig. 2A,B at a moderate pressure. Before measurement the cell was vacuum dried for 2 h at 60°C to release excess water.
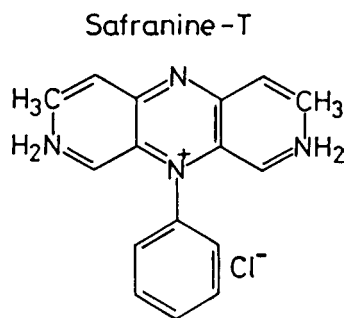
Safranine-T

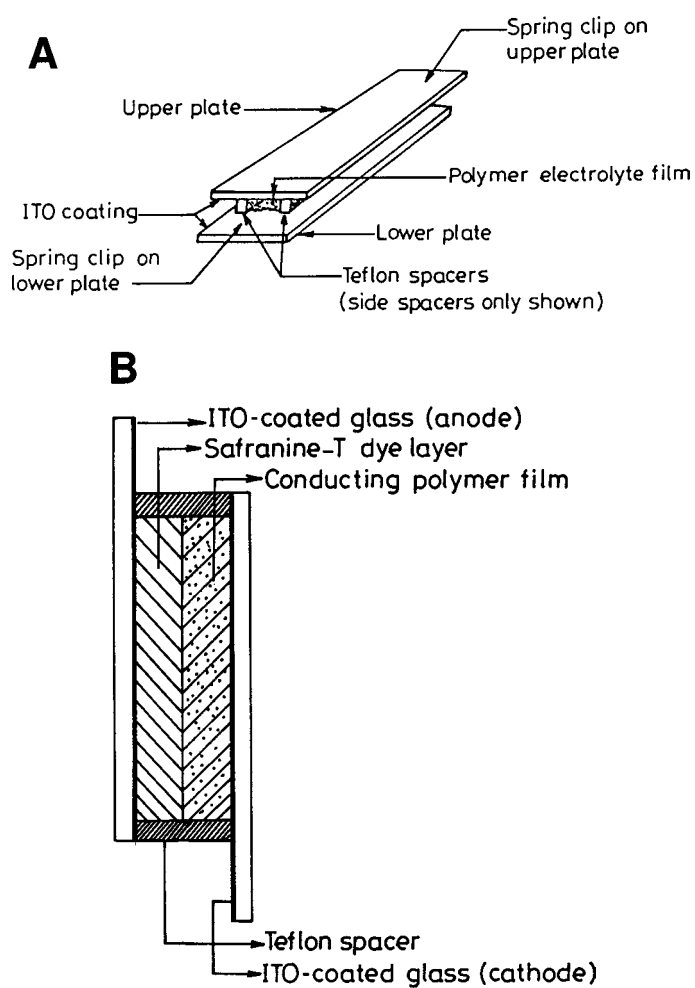Fig. 1. Structure of the Safranine-T dye.

Fig. 2. **(A)** Side view of the cell configuration. **(B)** Cross-sectional view of the cell configuration.
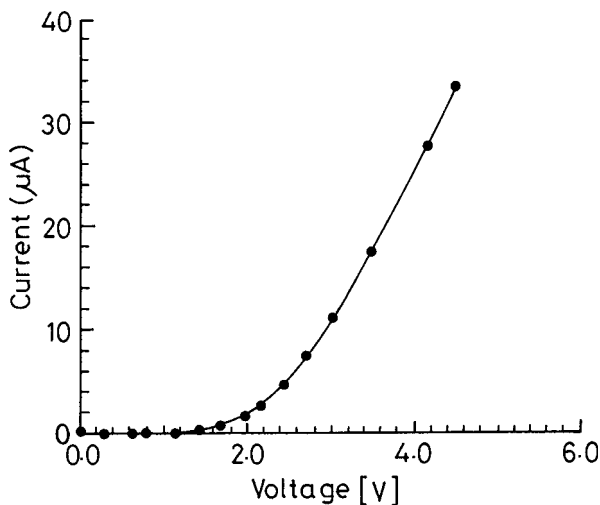
Fig. 3. Dark I-V characteristics of the device.

Dark Current-Voltage Characteristics

To study the dark current-voltage (I-V) characteristics, the film was biased by a direct current (DC) source with a series resistance of 47K. By varying the DC bias, the steady voltage across the series resistance is measured by a Philips $4\frac{1}{2}$-digit Multimeter. It was observed that the voltage took a lot of time (about 20 min) to reach the steady value after applying the DC bias voltage. The dark I-V characteristic is shown in Fig. 3.

The ln I-ln V plot shown in Fig. 4 indicates a change of slope at a bias voltage of 1.14 V, which seems to indicate that at this bias voltage a change in conduction mechanism occurs. As found in the literature *(19–21)*, the I-V characteristics can be fitted on the assumption that the electron travel from the lowest unoccupied molecular orbital states to the highest occupied molecular orbital states where they can be trapped in different trap levels below the lowest unoccupied molecular orbital states. Including the effect of these traps in the conduction processes, the I-V characteristics can be found to have the form $I \propto V^{m+1}$ in which $m = T_t/T$, with T_t being the characteristic temperature of the traps and T is the absolute temperature *(19)*. The relation has been tested by different researchers in different organic devices *(19–21)*. For thin layers, the value of m varies from 1 at low voltage to 8 ± 1 at high voltage, and for thick layers, m varies from 0 to 8 ± 1 *(21)*. With a suitable fit to our experimental data, we get a value of $m = 0.53$ for the applied voltage <1.14 V and $m = 3.71$ for the bias voltage >1.14 V to 4.5 V. The transport of charge carrier, its trapping, and recombination may be studied with the help of the model developed by Smith *(22)*.

Growth and Decay of Photocurrent

The cell was biased at a 2.2-V DC source making the ITO containing the dye film the anode with a series resistance of 47 K as before. After attaining
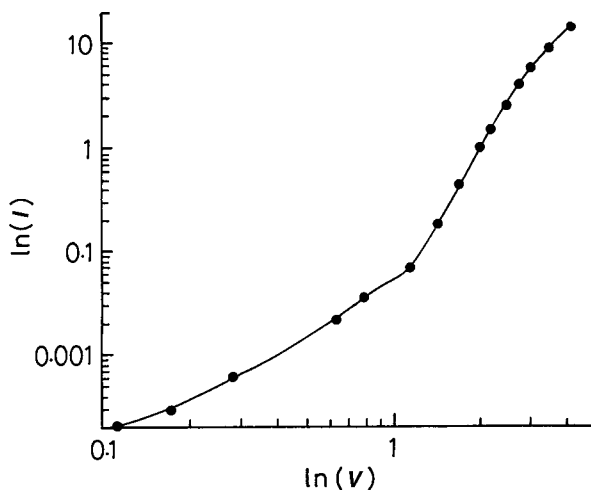
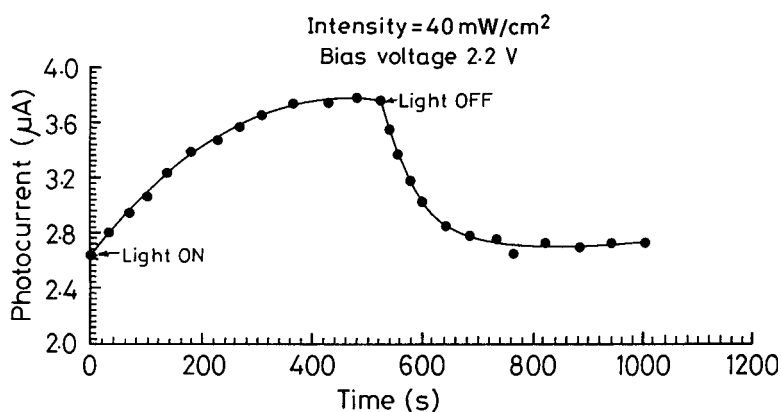Fig. 4. ln *I*–ln *V* plot of the dark I-V characteristics.

Fig. 5. Growth and decay of photocurrent with time for a particular bias voltage.

the steady value, the light from a 200-W tungsten lamp was allowed to fall on the device from the cathode side. The distance of the lamp was adjusted so that an intensity of about 40 mW/cm² measured by a lux meter (model 5200 with selenium detector; Kyoritsu Electrical, Tokyo) was incident on the device. Owing to this incident radiation, the voltage across the sensing resistance begins to rise. The growth of this photovoltage was recorded with respect to time. After a certain time the photocurrent is saturated. After attaining the saturation, the light was switched off. The reading of the multimeter begins to fall and returns to the initial value as in the dark condition. The total growth and decay of the photocurrent is shown in Fig. 5. The measurement was done a number of times with good reproducibility.
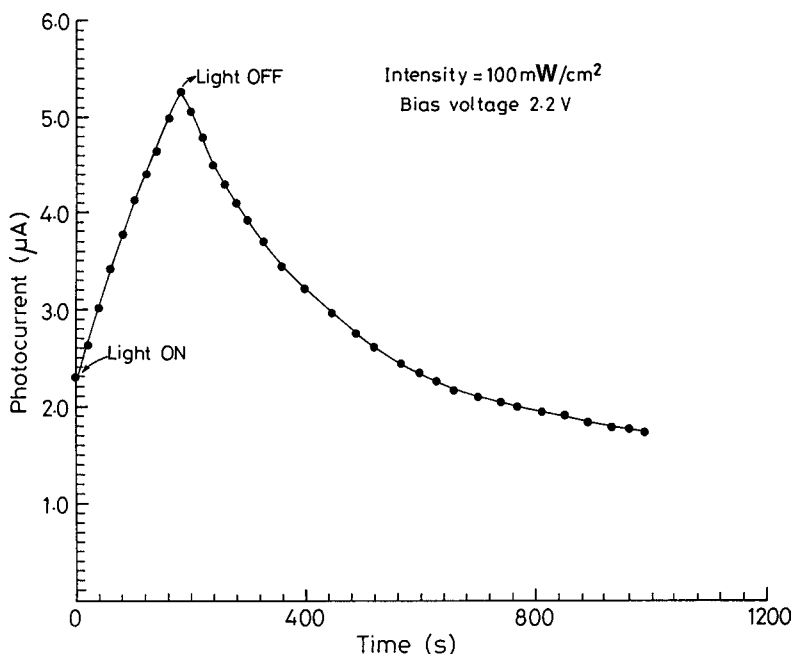
Fig. 6. Growth and decay of photocurrent with time for pulsed light.

Apart from the steady-state incident radiation, the optical response was also studied for a pulsed source radiation. An optical pulse of 200-s duration and intensity of about 100 mW/cm² was incident on the device for a bias voltage of 2.2 V. The growth and decay of the photovoltage is shown in Fig. 6. The relaxation time calculated from Figs. 5 and 6 is of the order of 200 s. This relaxation time is quite large, which indicates that the relaxation process is not electronic in nature but, rather, may be limited by ionic mobility. The detail of this photocurrent measurement have been described previously *(23)*.

Results and Discussion

We report herein the photoconductivity study of the thin film of Safranine-T dye and polymer complex in a qualitative way. In this device the Safranine-T dye is used as an optical sensitive material. The Safranine-T dye, being a cationic dye (the structure is shown in Fig. 1), leaves an excess hole (h^+) owing to the absorption of radiation. This charge is separated by the internal field produced by the redistribution of charges of the salt ion after application of the bias voltage. On application of the bias voltage, the cations and the anions move to the cathode and anode, respectively, which produces an internal field from cathode to anode. In the absence of the conducting polymer (i.e., absence of the internal field), it is observed that the photocurrent decreases instead of attaining saturation value, probably owing to the space charge effect.

All these preliminary experimental findings require quantitative explanation. Some attempts are being made in this direction. The most important aspect is to correlate the structure-property relation of the material. To correlate the structural property with the experimental facts, experiments have to be done using different materials. Presently, the mechanism for charge carrier generation in organic thin film optical devices is believed to be owing to the creation of bound electron-hole pairs and excitons by absorption of light in the photoactive parts of the devices. The charge generations occur as a result of dissociation of the excitons by interaction of the excitons with interfaces, impurities, or defects in high electrical fields. Application of two transparent electrodes make the device highly transparent. It may be expected that the quantum efficiency will increase if one uses one electrode with a reflecting coating instead of a transparent coating so that the incident radiation is confined inside the device owing to backreflection from the reflecting surface. The role of the conducting polymer is now under study. To estimate the internal field, the capacitance voltage measurement is presently in progress. Experiments to study the photocurrent growth with varying optical intensity and wavelengths are currently under way.

Acknowledgment

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