

Photocurrent growth and decay behavior of crystal violet dye-based photoelectrochemical cell in photovoltaic mode

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Received: 29 December 2010 / Revised: 5 May 2011 / Accepted: 22 May 2011 / Published online: 14 June 2011
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Abstract Crystal violet dye-doped photoelectrochemical cells (PEC) show different and unusual behavior in their electrical and optical characteristics. In this work, we have studied the photocurrent growth and decay behavior of crystal violet dye-based solid-state PEC in photovoltaic mode. Photocurrent growth and decay are studied for different intensities of illumination. They follow a power law relationship with time which is of the form $I_{\text{ph}} \sim t^{\pm\alpha}$, where I_{ph} is the photocurrent and α is a constant. The positive and negative signs are used to indicate the growth and decay of the photocurrent, respectively. This power law relation is explained by dispersive transport model which was originally developed by Scher and Montrol and subsequently modified by different workers. The constant, α is termed as dispersion parameter, and it is related to the disorder. It is observed that the value of this parameter depends on the intensity of incident illumination. Dependence of this dispersion parameter on incident intensity is studied in this work. Variations of α with intensity for growth and decay have been discussed. In our system, the value of α is 0.325 ± 0.005 for decay whereas, in the growth region, its value varies from 0.55 to 0.33, when intensity varies from minimum to maximum. The value of the disorder parameter, α , decreases as the intensity of illumination increases for growth of current whereas it remains nearly constant for decay of current. This work will

be helpful in understanding the charge transport mechanism of dye-based PEC cell.

Keywords Crystal violet · PEC · Photovoltaic current growth and decay · Charge transport · Disorder parameter

Introduction

Recently, organic materials are being widely used to develop different photovoltaic devices [1–4]. In Gratzel-type cells or dye-sensitized solar cells, different types of dyes are used to fabricate different type of solar cells ([5, 6]. The ionic conductivity [7, 8] in these photoelectrochemical cell (PEC) type plays a major role in enhancing the efficiency of the device. There are many advantages in the use of organic materials in solar cell fabrication. But, efficiency of the devices is quite low and shows different anomalous properties in its current–voltage (I-V) [9, 10] and photocurrent measurements [11–15]. Moreover, there are also difficulties in understanding the charge transport process due to the disorderly structure of organic materials. The effect of disorder is mainly responsible for showing these anomalous properties. However, these disorders may arise due to different reasons such as intermolecular arrangement, intramolecular disparities, etc. It will be useful if the effect of this disorder is estimated experimentally and is explained by any theoretical basis.

In this work, we have reported the photocurrent analysis of crystal violet (CV)-doped PEC. Different photo-physical properties of CV are widely studied in its aqueous solution. But, its behavior as photovoltaic material in PEC configuration is not well studied. The dye shows good optical response in solid-state form. To see the effect of the disorder, we have analyzed carefully the nature of the

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photocurrent behavior. We found that it follows the power law relation with time (t) of the form $I_{\text{ph}} \sim t^{\pm\alpha}$, where I_{ph} is the short circuit photocurrent and α is a constant. Positive and negative signs are used for growth and decay of photocurrent, respectively. By using the dispersive transport model developed by Scher and Montrol [16], the dispersion parameter is calculated for both growth and decay of current. The dependence of this parameter is studied with intensity.

Experimental

CV dye procured from S.D. Fine Chem. Ltd. is mixed with the solution of polyvinyl alcohol (PVA) procured from S.D. Fine Chem. Ltd., Boisar; M. W. 125000. To prepare the PVA solution, 5 g of PVA is taken in a cleaned test tube and mixed with 10 cc of double-distilled water. The mixture is warmed gently and stirred to make a transparent viscous solution of PVA. One milligram of CV is mixed with this solution.

A solid electrolyte was prepared in a separate cleaned beaker by mixing polyethylene oxide (PEO; BDH, England; M. W. 600000)–LiClO₄ (lithium perchlorate; Fluka, 99.5% pure)–EC (ethylene carbonate; Fluka, 99.5% pure)–PC (propylene carbonate; Fluka, 99.5% pure). The

complex of PEO–LiClO₄–EC–PC (30.60:3.60:19.60:46.20% by weight) were mixed, stirred, and heated at temperature 80 °C for 4 h. This gel-like solid electrolyte is mixed with the previously prepared dye–PVA solution to form the blend. This blend is heated at temperature 80 °C and stirred properly to mix them well for 2 h.

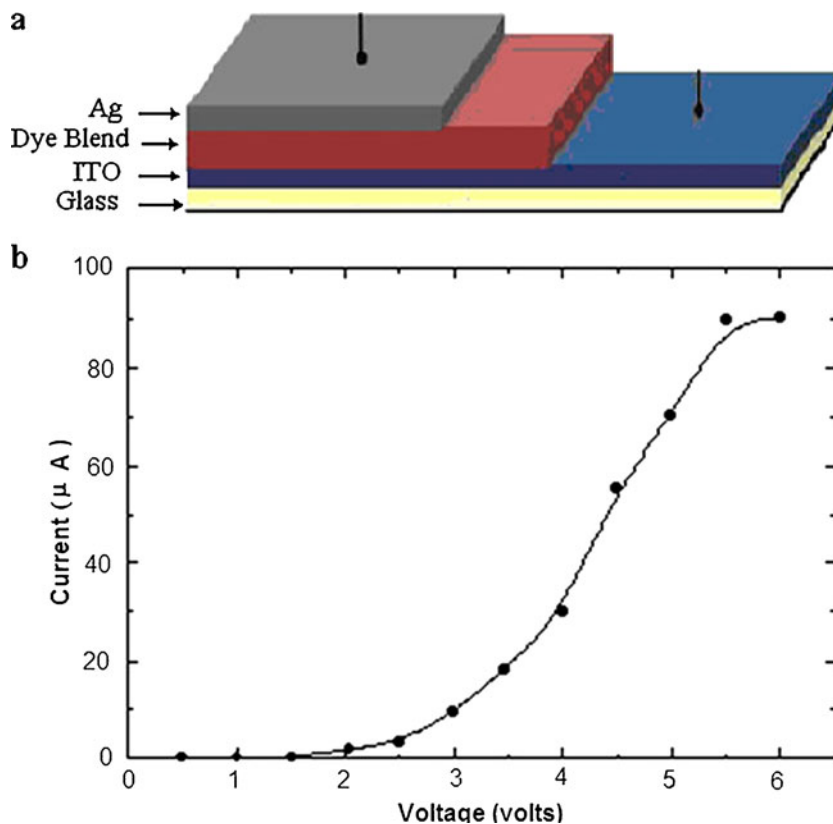
A solid film of this blend is sandwiched between a transparent indium tin oxide-coated glass plate and silver electrodes, which act as front and back contact electrodes, respectively. The cell structure is shown in Fig. 1a.

Dark I–V measurement was carried out. To measure the dark I–V characteristics, the cell is biased with a DC source with a series resistance of 56 K Ω . The current flowing through the device was estimated by measuring the voltage drop (measured by Agilent data acquisition unit, model no. 34970A) across this sensing resistance. The measured I–V data are shown in Fig. 1b.

For optical measurement, a tungsten lamp of 200 W is used. Light is allowed to incident on the cell. Varying the intensity of incident radiation by adjusting the distance between the source and the sample, the photocurrent is measured. The intensity is measured by a calibrated lux meter (Kyoritsu Electrical Instruments Works Ltd., Tokyo, model 5200).

The nature of photocurrent growth and decay is given in Fig. 2 for different intensities. The cell was connected for the measurement, and light is switched on after 100 s. Up to

Fig. 1 **a** Structure of the PEC cell and **b** current–voltage relation of the PEC cell



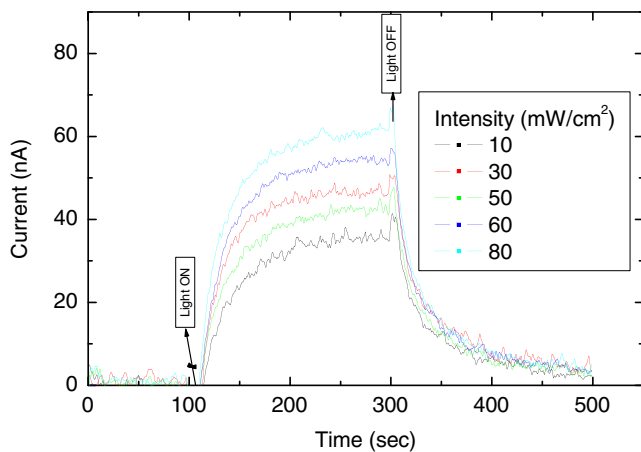


Fig. 2 Change of photocurrent with time for different intensity. Light is switched ON after 100 s and up to this portion, indicates the dark current. The current grows when the light is switched ON and becomes saturated after 200 s. After attaining the saturation, the light is switched OFF and photocurrent starts to decay and attains almost the initial dark value

100 s, the current is basically the dark current. After 100 s, as soon as the light is switched on, it is observed that the photocurrent starts to grow and the rate of current growth decreases and become saturated. After attaining the saturation value, the light is switched OFF and the photo current starts to decay and almost reaches the initial dark value.

Result

To analyze the behavior of the photocurrent, the growth and decay portion, the experimental curve of Fig. 2 is studied separately. In Fig. 3, only the growth part is shown for all

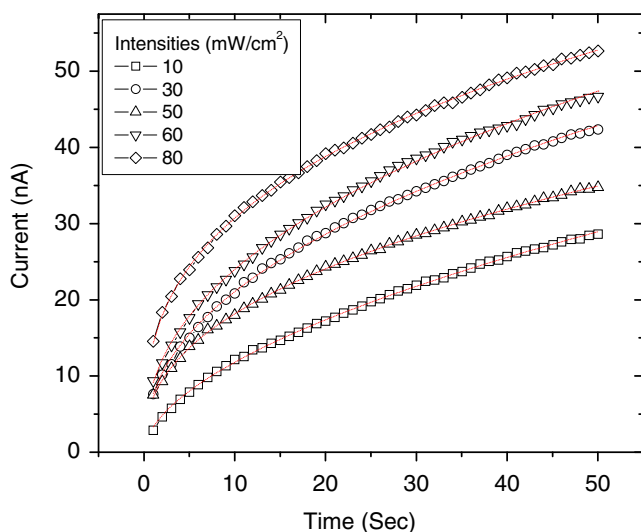


Fig. 3 The growth part of photocurrent for different intensity taken from Fig. 2. Only 50 data are taken after light ON position. Intensities are listed in the inset box

intensities. Logarithmic plot of this growth of current is shown in Fig. 4, and it clearly indicates the power law relation between current and time which is of the form, $I_{ph} \sim t^\alpha$. The value of α decreases with intensity. Values of α are 0.55, 0.44, 0.40, 0.42, and 0.33 for the intensities 10, 30, 50, 60, and 80 mW/cm^2 , respectively.

The decay portion of photovoltaic current is shown separately in Fig. 5. Logarithmic plot of this graph is shown in Fig. 6, and it also shows the power law decay of current with respect to time according to the relation $I_{ph} \sim t^{-\alpha}$. The value of α is 0.325 ± 0.005 , which does not vary significantly with intensity. The variation of α with intensity is shown in Fig. 7 for both growth and decay, respectively. It is seen that, for the growth of current, there is strong dependence of this parameter whereas the variation of this parameter is not so significant for the decay of current. During the growth, the charge carriers are generated, and there is a dynamic equilibrium between the charge generation and recombination processes. When the current is saturated, it is expected that the rate of charge generation and recombination processes become equal and a static equilibrium is established. During decay, the charge generation process is absent and only the recombination processes become dominant. During this charge relaxation processes, the dispersion parameter does not affect significantly whereas the generation process has a strong dependence on the dispersion transport processes.

From these experimental results, it is clear that the dependence of photocurrent growth and decay with time follows power relation for CV dye-doped PEC structure. This unusual nature may be attributed to the disorder nature of the system. The device is disorder in nature like other devices made from organic materials. Due to disorder, they

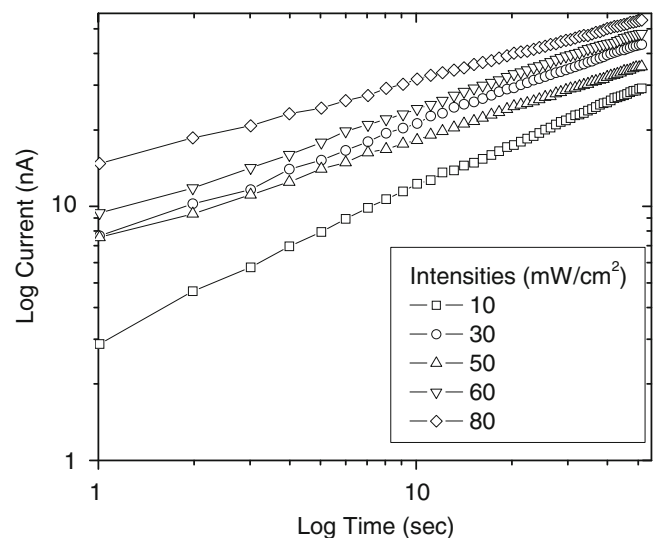


Fig. 4 Logarithmic plot of photocurrent growth and time for different intensity taken from Fig. 2

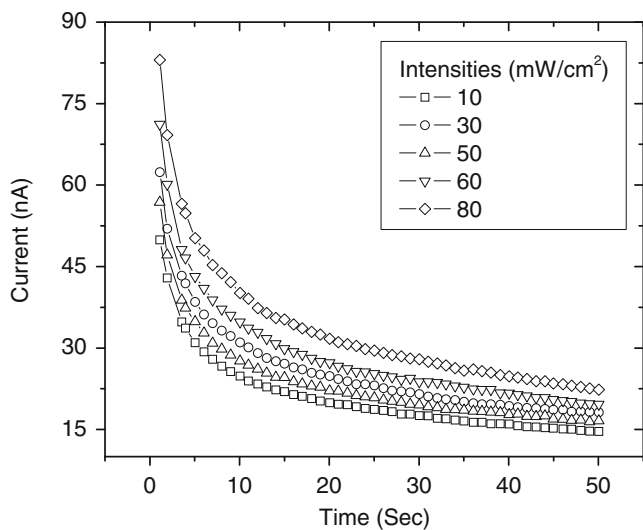


Fig. 5 Decay portion of photocurrent for different intensities. Data are taken from Fig. 2. Only 50 data are taken after light OFF position. Intensities are listed in the inset

are prone to have traps, and these traps play major role in charge transport process. In the proceeding section, we present a theoretical model to understand qualitatively the power law nature of current growth and decay. As indicated in the earlier section, this model was originally developed by Scher and Montroll [16] to explain the photocurrent nature of a-Se.

Theoretical model

In order to explain the charge transport in such system, a dispersive model is used which was originally suggested by Scher and Montroll [16] and has been further developed by

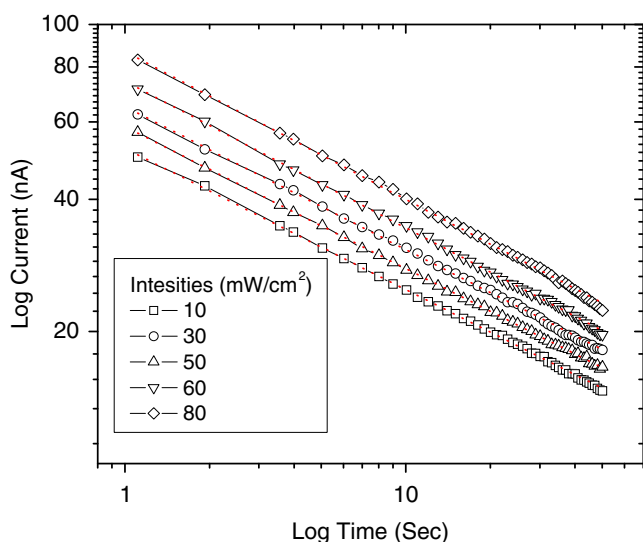


Fig. 6 Logarithmic plot of photocurrent with time. Data are taken from Fig. 2

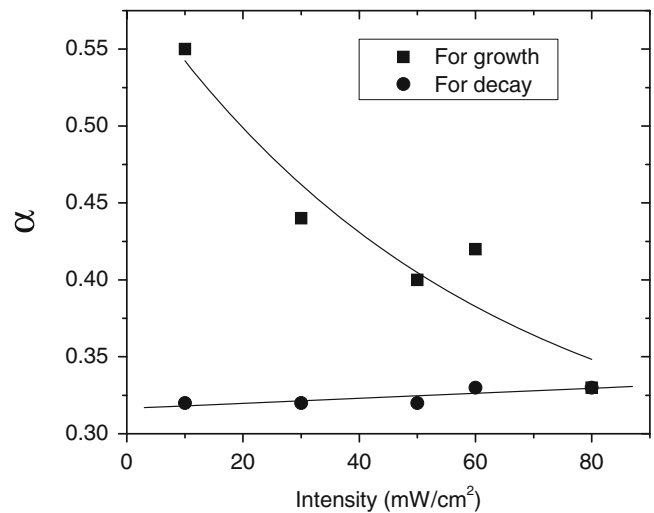


Fig. 7 Variation of α for both growth and decay of photocurrent. α decreases with the increase of intensity and nearly constant for decay of current

different workers [17–20]. The system is considered as a disorder one having distribution of scattering (or trap) centers. The charge carriers are highly localized. During transport, the charge trapping occurs via hopping process. The motion of a carrier hopping through a random array of sites is presented in Fig. 8. Carriers hop through a random array of different localized sites shown by the arrow. There will be distribution of the energy levels of the localized hopping sites along with a distribution in the intersite separation between these localized states. As a result, there is a distribution of hopping times. Both the factors, i.e., distribution of the energy levels and distribution in the intersite separation distances, strongly affect the hopping time.

A distribution function, $\psi(t)$, as suggested by Scher and Montroll [16], may be written in the following form,

$$\psi(t) \sim t^{-(1+\alpha)} \text{ where } 0 < \alpha < 1 \tag{1}$$

Where t is time and α is the dispersion parameter and essentially a measure of dispersivity.

It is further mentioned here that this form of waiting time distribution essentially arises from an exponential distribution of trap states [21, 22] of the following form,

$$N_t(\varepsilon) = N_0 \exp\left(-\frac{\varepsilon}{kT_c}\right) \tag{2}$$

Where subscripts t refers to traps and T_c represents the characteristic temperature and ε is the traps energy. Immobilization time of a trapped carrier is equal to the thermal release time, t which is,

$$t = \nu^{-1} \exp\left(\frac{\varepsilon}{kT}\right) \tag{3}$$

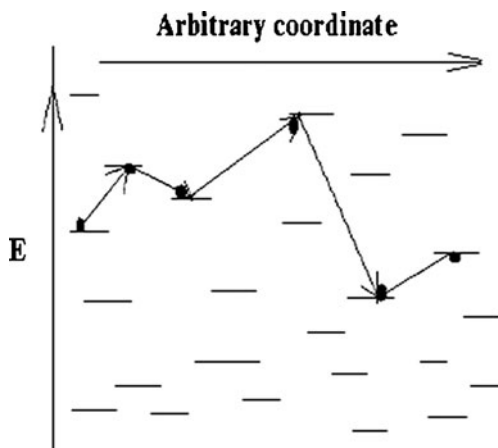


Fig. 8 Schematic representation of carriers hopping through a random array of sites

Where ν (per second) is the attempt-to-escape rate. Assuming all the traps have same cross-section, the distribution time is given by,

$$\psi(t) = \frac{N_t(\varepsilon)}{kT_c N_0} \frac{d\varepsilon}{dt} = \alpha \nu (t\nu)^{-(1+\alpha)} \tag{4}$$

for $t > \nu^{-1}$ where $\alpha = T/T_c$.

This is the expression of the distribution function given in Eq. 1. So, it can be said that a distribution function used in our model essentially indicates an exponential distribution of trap states.

Now, in order to describe the photocurrent behavior of our experimental results, the mobility (μ_D) may be written in the following form,

$$\mu_D(t) \propto \mu_0 t^{(\alpha-1)} \tag{5}$$

where μ_0 is the free carrier mobility. The standard form of the photocurrent is written as a function of time as follows

$$I_{ph}(t) = N(t) q E \mu_D(t) \tag{6}$$

where $N(t)$ is the concentration of carriers in the sample, q is the electronic charge, E is the electric field and $\mu_D(t)$ is a time-dependent mobility defined by Eq. 5.

Kurtz and Huges [17] have utilized the above dispersive transport model to derive an expression for the growth of photocurrent. In our earlier work [15], the growth and decay behavior of this photocurrent has been described. For the completeness of the present discussion, part of it is being repeated here.

The photocurrent generated in a sheet of thickness dx and irradiated by a pulse of duration ε , called pulsed surface excitation be

$$I(t) = I_0 \varepsilon t^{-(1-\alpha)} \frac{dx}{L} \text{ for } t < T_t \tag{7a}$$

$$I(t) = I_0 \varepsilon T_t^{2\alpha} t^{-(1+\alpha)} \frac{dx}{L} \text{ for } t > T_t \tag{7b}$$

For pulsed bulk excitation, integrating the above equation over the sample thickness the photocurrent can be written as

$$I(t) = I_0 \varepsilon t^{-(1-\alpha)} \left[1 - \frac{2}{3} \left(\frac{t}{T_t} \right)^\alpha \right] \text{ for } t < T_t \tag{8a}$$

$$I(t) = I_0 \varepsilon T_t^{2\alpha} \frac{t^{-(1+\alpha)}}{3} \text{ for } t > T_t \tag{8b}$$

For continuous bulk excitation the photocurrent can be written as

$$I(t) = I_0 \frac{t^\alpha}{\alpha} \left[1 - \frac{1}{3} \left(\frac{t}{T_t} \right)^\alpha \right] \text{ for } t < T_t \tag{9a}$$

$$I(t) = I_0 \frac{T_t^\alpha}{\alpha} \left[1 - \frac{1}{3} \left(\frac{T_t}{t} \right)^\alpha \right] \text{ for } t > T_t \tag{9b}$$

When the radiation is turned on at time $t=0$ and T_t is a characteristic time.

So, for continuous radiation, we may qualitatively write from Eq. 9a for the growth of photocurrent with time approximately as

$$I_{ph}(t) \sim t^\alpha \quad t \ll T_t \tag{10}$$

which is of the same form as found in power law fitting of our experimental result.

Equation 10 qualitatively explains the nature of photo-voltaic current growth. Our experimentally found power law relation exactly fitted with this equation.

The decay of the photocurrent and dark discharge have been studied by different workers [7, 9]. The sample sandwiched between two electrodes may be assumed as plane parallel capacitors. Due to illumination, the charge carriers are being stored. At the moment, when light is switched off, the photocarriers within the sample become maximum which contributes a maximum photovoltage. It is expected that, due to sudden change, i.e., switching off the illumination, the surface charge changes drastically with time. The stored charges start to decay. These charge carriers become trapped during transport. The transient current analysis accounts for the time-dependent flow of charge carriers under the applied bias in the presence of traps, space charges, etc. The Poisson's equation is solved for both free and trapped charges with suitable boundary conditions. The change of photovoltage with time may be approximated as

$$V(t) = \left(\frac{L^2}{2\mu_D} \right) t^{-1} \tag{11}$$

Where $V(t)$ is photovoltage, L is the thickness of the device, μ_D is time-dependent mobility.

Taking $\mu_D(t) \propto \mu_0 t^{(\alpha-1)}$ for dispersive transport in disorder amorphous system one gets from Eqn. 11.

$$V(t) \sim t^{-\alpha} \quad (12)$$

The photocurrent is measured across the sensing resistance. So, the photocurrent is proportional to voltage across the resistance, and it can be expressed as

$$I_{ph}(t) \sim t^{-\alpha} \quad (13)$$

Thus, the power law photocurrent decay in our reach system may be qualitatively explained by using Eq. 13.

The Eqs. 10 and 13, as deduced from theoretical model, qualitatively describe the behavior of the photocurrent during growth and decay, respectively.

According to the model, α is dispersion parameter and is a measure of disorder of system concerned. Its value lies between 0 and 1, lower value of α indicates more disorder system. One important point may be noted here that these equations were used in our earlier work [15] to explain the photocurrent growth and decay for safranin-T-dye-based PEC where the measurement was done in photoconducting mode. The same theoretical idea is also applicable for photovoltaic measurements of CV dye-based PEC.

Conclusion

CV dye-based PEC shows photovoltaic effect. To enhance the quantum efficiency and to understand the device mechanism, the charge transport study is informative. In this work, the growth and decay of photocurrent is studied for CV dye-based PEC. Experimental results show that the photocurrent growth and decay nature is best fitted with power law relation with time. This unusual nature of photovoltaic current growth and decay has been discussed using the dispersive transport model, which was originally developed by Scher and Montroll for a-Se system under pulsed light with slight modification. By comparing experimental results and theoretical model, we have estimated the dispersion parameter α and its dependence

with incident intensity. From the definition of α , it is clear that lower value of α makes the system more disorderly. For photocurrent growth, we found that α decreases as intensity increases whereas its value is nearly constant for decay processes of photocurrent. This nature of dependence needs more attention for future study.

Acknowledgment We are grateful to Prof. S.C. Bera, Dept. of Chemistry, Jadavpur University, for providing valuable suggestions throughout this work. The authors are also thankful to Department of Science and Technology, India, for financial assistance.

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