Estimation of trap energy of fuchsin dye sensitized Organic Photovoltaic Device based on Titanium Dioxide (TiO_2)

Dipankar Sahoo[1], N. B. Manik[2]*

[1]*Department of Physics, Condensed Matter Physics Laboratory, Jadavpur University, Kolkata- 700 032*

Email: dipankarsahoo93@gmail.com

Abstract

Recently, dye sensitized photovoltaic cell plays an important role as a renewable source of energy because of low material cost, easy processing techniques. But the organic devices are prone to traps due to which charge carriers get trapped or recombined within the device before collection at the electrodes. So traps limit the device performance. The study on the charge transport mechanism enables us to estimate this trap energy. In this work, we have designed the photovoltaic device and estimated the trap energy of inexpensive water-soluble Fuchsin dye based photovoltaic cells. To design a photovoltaic device we have used ITO as a front electrode and copper as a back electrode. 540mg of TiO_2 nanoparticles and 100mg of Fuchsin dye mixed well in N, N-Dimethyl formamide (DMF). A thin layer of this TiO_2 nanoparticles and dye has been deposited between two electrode using popular method named doctor's blade method. A drop of electrolyte made of lithium percolate ($LiClO_4$), ethylene carbonate (EC) and propylene carbonate (PC) solution has been used to obtain better device performance. The analysis of dark current density- voltage (J-V) characteristics using exponential charge transport mechanism of this photovoltaic cell the trap energy has been calculated 0.5399 ± 0.006 eV. Also, we have observed photovoltaic effect of this device. Under illumination of 120 kLUX intensity, maximum short circuited current density is obtained 4.62 $\mu A/cm^2$ and open circuited voltage is 0.24 Volt.

Keywords: *Fuchsin dye, trap energy, short-circuited current density, open-circuited voltage.*

5. Introduction

In recent decades, organic photovoltaic cells (OPV) have drawn attention due to their easy fabrication process, large-scale and low-cost production and easily tunable band structure of organic materials [1, 2]. But the long-term stability and power conversion efficiency of OPV are quite low compared to its inorganic counterpart. From literature reviews, it has been seen that most of the objectives of the researchers in this area is to discover the best device configuration and find the best material composition that can increase the stability and energy conversion efficiency of OPV devices. The selection of new dyes, the use of different device structures and the incorporation of nanoparticles are the different techniques used in this direction [3]. In 2019, a group of researchers reported an energy conversion efficiency of 17.29% for a two-terminal monolithic solution tandem OPV [4]. Recently, IIT Hyderabad has reported that the New Fuchsin (NF) organic dye-based device shows a good photovoltaic effect in the presence of TiO_2 nanoparticles [5].

In this work, we have studied the electrical and light effect of Fuchsin dye in the blended structured device in the presence of TiO_2 nanoparticles. Fuchsin dye is generally used in spectroscopy during staining. But as photoactive material, Fuchsin dye is one of the least reported dyes. The role of TiO_2 is widely accepted as an acceptor in many literatures [6, 7]. In this work, a very well-known solvent namely N, N-Dimethyl formamide (DMF) has been chosen to prepare the solution. The Fuchsin dye and the TiO_2 nanoparticle are dissolved in N, N-Dimethyl formamide (DMF) and stirred on a magnetic stirrer for one hour. This mixed solution has been used to make a film on the front electrode i.e. glass plate coated with indium tin oxide (ITO) and on the back electrode i.e. copper plate using the Doctor's blade technique [8]. Then two electrodes are placed together to obtain a blended structured device. The characteristics of I-V of the device has been measured with the help of Keithley 2400 SMU. The trap energy of the prepared device has been calculated from the analysis of the J-V characteristics. In addition, the transient effect of the cell has been studied in this work.

2. Experimental section

2.1. Materials

Fuchsin dye has purchased from Loba Chemie Pvt. Ltd., Mumbai, India. 99.5% pure grade. TiO_2 and ITO have procured from Sigma - Aldrich. Fig. 1.(a) shows the structure of Fuchsin dye. Solvent N, N-Dimethylformamide (DMF) procured from Merck Specialties Private Limited, Mumbai, India. In this work ITO coated glass has used as a front electrode and copper sheet has used as a back electrode.

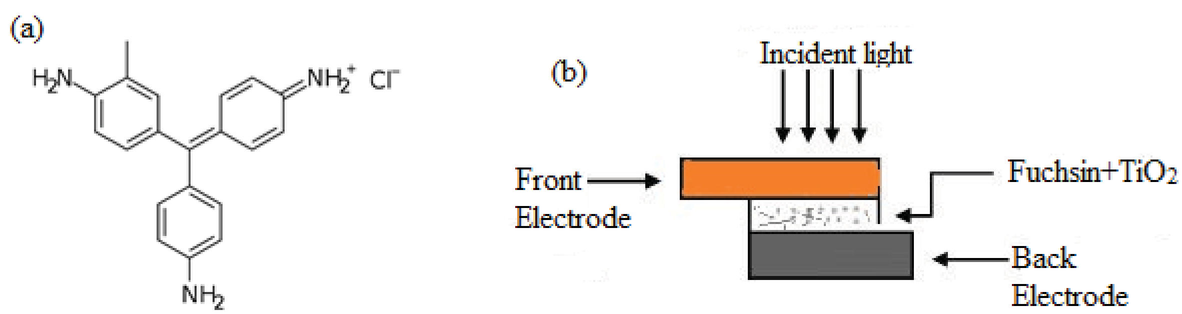

FIG. 1. (a) Chemical structure of Fuchsin dye used as photoactive material [9] and (b) Device structure.

As mentioned earlier, Fuchsin dye has been chosen because it has a good optical response but in OPV mode it is one of the least reported dye. Fuchsin with molecular formula $C_{20}H_{19}N_3{\cdot}HCl$ (Rosaniline hydrochloride) is a typical magenta dye. In general, Fuchsin is used to stain bacteria and sometimes as a disinfectant. Its color originates from the absorbance in the visible region of the spectrum due to the delocalization of electrons in the solvent. In addition to this, it is a low cost and commonly available dye. Moreover, this dye is soluble in water and organic solvents. The absorption spectra of Fuchsin dye in different solvents are shown in Fig. 2. In DMF, this Fuchsin dye has the absorption peak at almost 560 nm which is maximum. For this reason we have chosen DMF as solvent in this work.

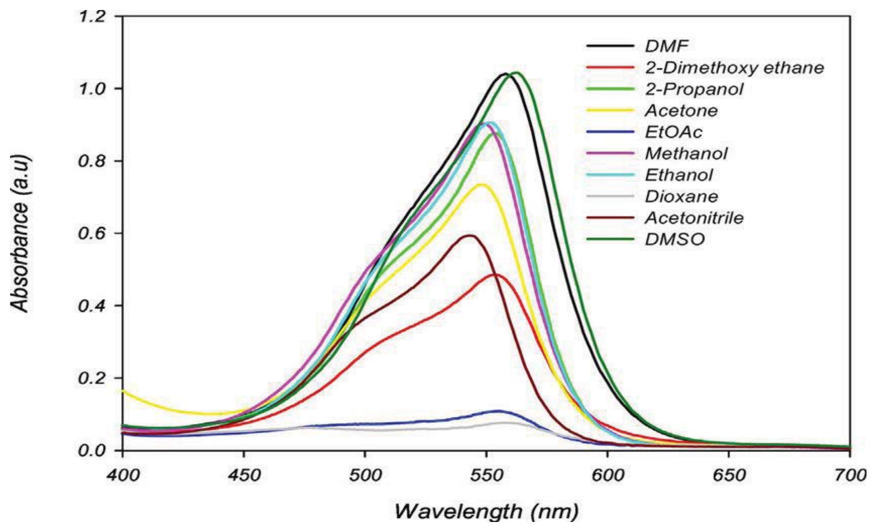

FIG. 2. Absorption spectra of fuchsin dye [9]. In DMF solvent it has maximum absorbance at wavelength 560nm.

2.2 Film preparation and device fabrication

For preparing the electrodes, the glass coated with indium tin oxide (ITO) and the copper plate has been first cleaned in acetone then in ethanol and finally in deionized water. A Dhona 100 DS high precession weighing scale has used to measure 540 mg of titanium dioxide (TiO_2) and 100 mg of Fuchsin dye. Therefore, both the TiO_2 nanoparticle and the dye have dissolved in 3 ml of DMF. The mixture has been stirred for one hour using a standard magnetic stirrer. The resulting solution (80 µL) has deposited on the ITO electrode using a well-known doctor blade technique. In the next step, two electrodes combine to form a device. The schematic structure of the device has been shown in Fig. 1(b). The device has been kept in a vacuum desiccator for 6 hours. After 8 hours from the beginning of the preparation of the film, the characterization of the device has begun. Before beginning the characterization, a drop of electrolyte previously prepared from lithium percolate ($LiClO_4$), ethylene carbonate (EC) and propylene carbonate (PC) has been used.

2.3 Characterization

The current density-voltage (J-V) relationship of the prepared device has been measured with a Keithley 2400 source measurement unit. For the dark J-V measurement of the device, a positive potential has been given to the ITO electrode and a negative potential to the copper electrode. The potential has been varied from 0 to 4 volts in small 0.5 volt steps with 30 seconds of delay in our experiment. Experimental data has recorded in the open environment at a temperature of 26 ° C.

2.4 Result and Discussion
2.4.1 Dark I-V characteristic

Fig. 3. shows the dark J-V characteristics of the prepared cell. It is observed that the dark current of the cell has two distinct regions. The observation shows that beyond a certain transition voltage (V_{th}), the current conduction mechanism changes for the cell.

To analyse the device's charge transport mechanism, we have considered an exponential trap state distribution for our system. The exponentially distributed trap charge concentration g (E) expressed as [10]

$$g\,(E) = \frac{N_t}{k_B T_t}\exp\left(\frac{F_n}{k_B T_t}\right) \qquad (1)$$

$$= H_n \exp\left(\frac{F_n}{k_B T_t}\right)$$

Where $H_n = \frac{N_t}{k_B T_t}$, T_t is the characteristic temperature, k is Boltzmann constant and E is the Fermi energy.

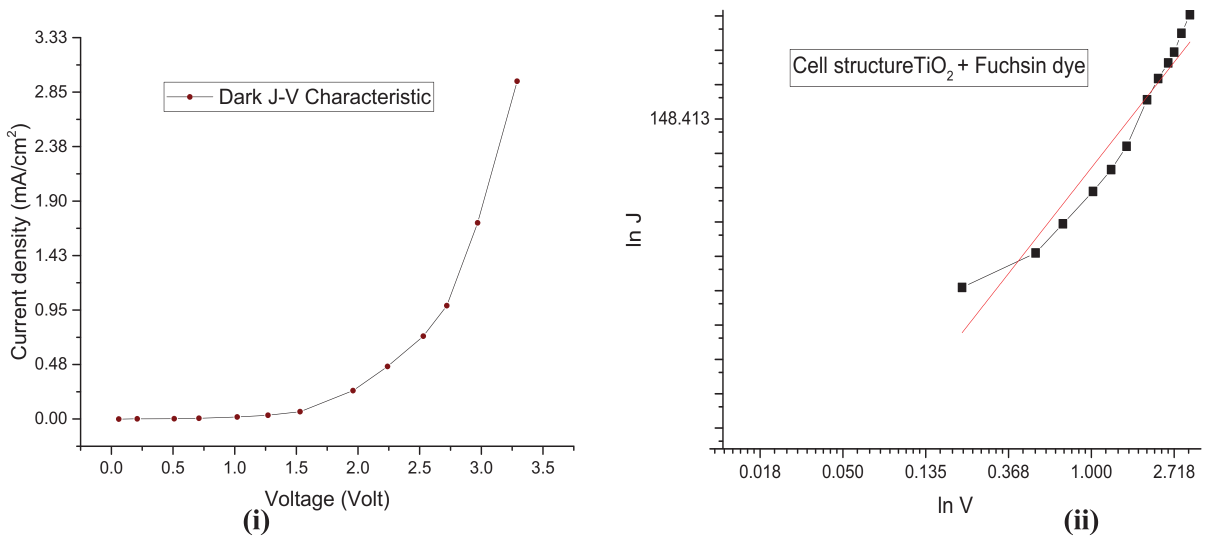

FIG 3. (i) J-V characteristics and (ii) InJ-InV characteristics for Fuchsin dye based device.

Considering Equation. (1) the current density relation is readily approximated by,

$$J_t = N_c\,\mu q^{1-m}\left(\frac{m\varepsilon}{H_n(m+1)}\right)^{m}\left(\frac{2m+1}{m+1}\right)^{m+1}\frac{V^{m+1}}{L^{2m+1}} \qquad (2)$$

Where V is the voltage. We see that in this region the current density-voltage characteristics follows a power law relationship: $J \sim V^{m+1}$, where $m = T_t/T$, T is absolute temperature. Then the trap energy is given by the relation,

$$Ec = kT_t$$

$$= kmT \qquad (3)$$

Table 1. Extracted values from lnI- InV curve

Cell structure	Value of m above V_{th}	Trap energy E_c (eV)	Error in trap energy
TiO_2 + Fuchsin dye	2.07684 ± 0.25599	0.5399	± 0.006 eV

2.4.2 Photo effect measurement

Two important parameters of any PV cells are the short circuited current density and open circuited voltage. In our photo effect measurement the value of these two parameters have been measured by shorting two terminals of the device while measuring short circuited current density and keeping open two terminals of the device while measuring open circuited current density. The short circuited current density and open circuited voltage has been measured 4.62 μA/cm^2 and 0.24 Volt respectively.

To observe the transient characteristics of the prepared cell, we have plotted the growth and decay of the photocurrent density with reference to time. Fig. 4 represents the current density behavior in the presence and absence of light. In this measurement, the cell has been exposed to a fixed light intensity of 120kLUX recorded by a METRAVI Model-1334 standard lux meter. The maximum current reached after 53 seconds of lighting, that is, the time required for the photocurrent to grow. After the maximum current reached, the light switch has turned off and the time required to reach the current from where it began to grow is 55 seconds.

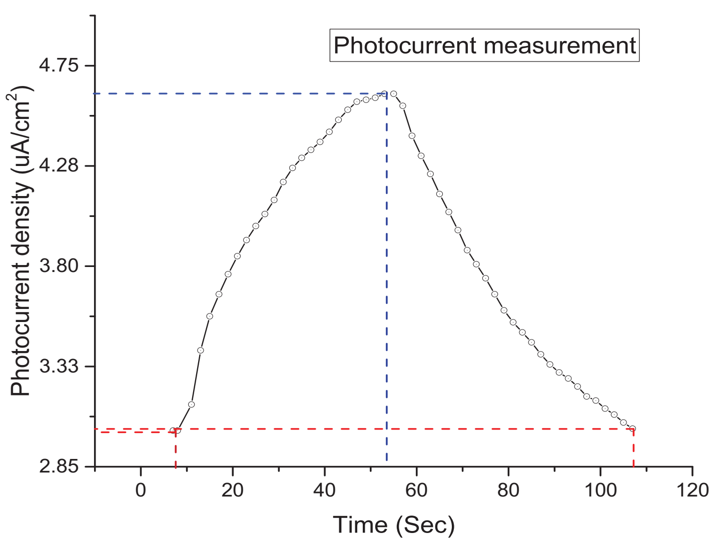

FIG 4. Photocurrent density growth and decay characteristics of the cell.

3. Conclusion

An attempt has been made to determine the trap energy and to observe the photo effect of the Fuchsin dye-based photovoltaic device in the presence of TiO_2 nanoparticles. In the previous work, IIT Hyderabad reported that they have developed New Fuchsin based PV device using TiO_2 nanoparticles. But there has been no mention of concentration of trap in the work though we all know organic materials are prone to trap. In our work, we have calculated trap energy. According to our calculation, we have seen that the value of trap energy is too high. This high trap energy indicates that the charge carriers generated within the cell are getting trapped before they collected at the electrodes. As a result, we are not getting the value of the short circuited current and the open circuited voltage as expected. But the growth in photocurrent indicates that the device performance can be improved further by reducing trap energy. We believe that our work will be useful in future research on photovoltaic devices based on fuchsin dyes.

4. Acknowledgement:

The author sincerely acknowledges Department of Science & Technology (DST), Government of India for financial assistance and one of authors, Dipankar Sahoo is thankful to DST for awarding a INSPIRE research fellowship.

REFERENCES

[1] M. Wright, A. Uddin, et. al. "Organic-inorganic hybrid solar cells: A comparative review", *Solar Energy Materials and Solar Cells*, 107, 87-111, (2012).

[2] U. Zhokhavets, T. Erb, G. Gobsch, et. al.,"Relation between absorption and crystallinity of poly(3-hexylthiophene)/fullerene films for plastic solar cells", *Chemical Physics Letters*, 418, 347–350, (2006).

[3] S. Chakraborty, N. B. Manik , "Effect of single walled carbon nanotubes on the threshold voltage of dye based photovoltaic devices", *Physica B*, 481, 209-216, (2016).

[4] M. Lingxian, Y. Zhang et. al. "Organic and solution-processed tandem solar cells with 17.3% efficiency", *Science*, 361, 1094–1098, (2018).

[5] R. Kokal., S. Bhattacharya et. al., "Low Cost 'Green' Dye Sensitized Solar Cells Based on New Fucshin dye with Aqueous Electrolyte and Platinumfree Counter Electrodes", *Solar Energy*, 188, 913-923, (2019).

[6] Y. Bai, I. Mora-sero et. al. al.,"Titanium Dioxide Nanomaterials for Photovoltaic Applications", *Chem. Rev*., 114, 10095-10130, (2014).

[7] E. Gondek, Y. Djaoued, J. Robichau et. al., "Influence of TiO2 nanoparticles on the photovoltaic efficiency of the ITO/PEDOT: PSS/fluorine copolymers/polythiophene: TiO2/Al architecture", *Journal of Materials Science: Materials in Electronics*, 23, 2057–2064, (2012).

[8] T. Huynh, T. Hoang et. al., "Preparation of TiO2 thin film using modified doctor-blade method for improvement of dye-sensitized solar cell," *34th IEEE Photovoltaic Specialists Conference (PVSC)*, Philadelphia, PA, 002168-002171, (2009).

[9] J. P. Graham, M. A Rauf et. al. “Spectral behavior and computational studies of fuchsin in various solvents”, *Journal of Molecular Liquids*. 238, 193-197, (2017).

[10] S. Chakraborty, N. B. Manik “Effect of COOH-functionalized SWCNT addition on the electrical and photovoltaic characteristics of Malachite Green dye based photovoltaic cells”, *Journal of Semiconductors*, 35, 124004-1, (2014).