Study on the Effect of Zinc Oxide Nanoparticles on Injection Barrier Height of Crystal Violet Dye Based Organic Device

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Abstract

Organic devices have achieved substantial progress due to its flexibility, cost effectiveness, simple processing and wide customizability. But there are certain limitations of these devices. One of the main limitations is the lower charge injection from metal electrodes to the organic layer which affects the performance of these devices. The charge injection process is strongly dependent on the injection barrier height at metal- organic layer interface. Due to high barrier height at metal – organic layer interface, the charge injection is reduced at the interface. Attempts need to be made to reduce the injection barrier height at metal – organic layer interface to improve the charge injection process. In the present work, we have studied the injection barrier height of Indium tin oxide coated glass/Crystal violet dye/Aluminium based organic device and subsequently we have also observed the effect of zinc oxide nanoparticles on injection barrier height of this device. Indium tin oxide coated glass and aluminium are used as front electrode and back electrode respectively to form this device. The device has been prepared with and without zinc oxide nanoparticles by using spin coating technique. We have analyzed the steady state current-voltage characteristics of the device to determine the barrier height of the device. Barrier height is reduced from 0.87 eV to 0.78 eV in the presence of zinc oxide nanoparticles. The barrier height is also estimated by using another alternative method which is known as Norde method. By using Norde method, barrier height is measured which reduces from 0.83 eV to 0.77 eV in presence of zinc oxide nanoparticles. Both the methods show good consistency with each other. Reduction of the injection barrier height in presence of zinc oxide nanoparticles indicates better charge injection through the metal - organic dye interface. The higher electron mobility of zinc oxide nanoparticles facilitates efficient charge injection at the interface. Thus, this work will be informative to study the effect of zinc oxide nanoparticles on injection barrier height as it reduces the barrier height to improve the charge flow at metal – organic dye interface.

Keywords: Crystal Violet Dye, Injection Barrier Height, Metal – Organic Dye Interface, Zinc Oxide Nanoparticles.

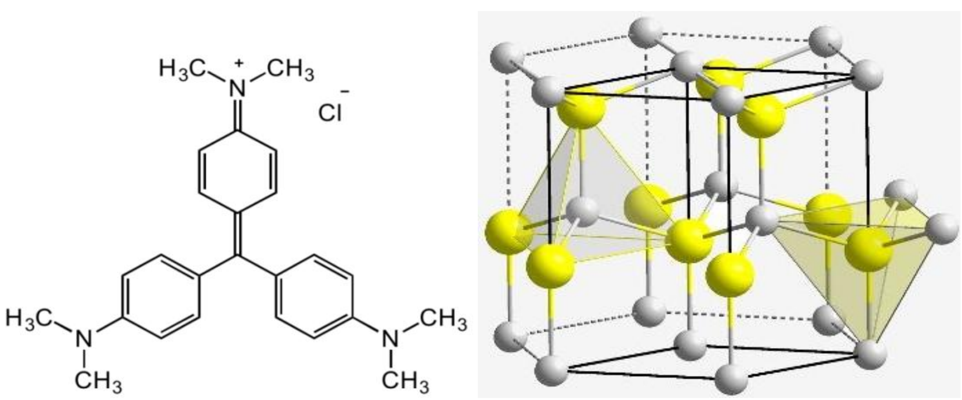
1. Introduction

The organic materials are becoming one of the best candidates for becoming the material platform for the development of more flexible, light weight and cost effective electronic devices [1]. One of the distinguishing features of the organic device is that they are composed of molecules which held together by van der Waals force. Due to which, weak electronic interactions among the molecules of these organic devices exist [2]. One of the main limitations of these organic devices is poor charge injection at metal-organic layer interface which can be attributed to the high injection barrier height at the interface. It is of paramount importance to decrease the injection barrier height at the interface in order to improve the charge injection process as the charge injection process is strongly dependent on the injection barrier height at metal- organic layer interface [3]. Injection of charges at the metal-organic layer interface has also significant influence on the electrical properties of these organic devices [4]. In this work, we have estimated the barrier height of Indium Tin Oxide (ITO) /Crystal Violet (CV) dye/Aluminium (Al) based organic device and also observed the effect of zinc oxide nanoparticles (ZnO) on the injection barrier height at the metal – organic layer interface. We have calculated the injection barrier height at the metal – organic layer interface from steady state current – voltage (I –V) characteristics of the device and also by using another method namely Norde method. It has been observed that both the methods show decrease in the barrier heightat the metal-organic layer interface in the presence of zinc oxide nanoparticles. The higher electron mobility of zinc oxide nanoparticles facilitates efficient charge injection at the interface [5]. Reduction of the injection barrier height at the metal – organic interface implies better charge injection at the interface and can also be related to the improved conductivity of the device.

The charge injection barrier at the interface between a metal and organic material can commonly be described by the interfacial barrier height of metal to semiconductor contact. Injection current usually consists of thermionic-injection current and fieldinduced tunneling current. In this case of low voltages, tunneling injection is negligible and thermionic emission dominates. Thus,we have analyzed the charge injection mechanism of the device at metal – organic layer interface by using Richardson – Schottky (RS) model of thermionic emission [6].

2. Materials and Sample Preparation

Crystal Violet (CV) dye is not only used as a textile dye, but also it is used to dye paper and as a component of navy blue and black inks for printing, ball-point pens, and inkjet printers. This dye is also used as a histological stain, particularly in Gram staining for classifying bacteria. In our work, CV dye is procured from LobaChemie Private Ltd, India. This dye with chemical formula [$C_{25}N_3H_{30}Cl$] is a cationic dye that dissociates in aqueous solution to give a positively charged coloured ion[7]. Fig. 1(a) shows the structure of CV dye. In this work, we have incorporatedZnO nanoparticles in the CV dye based organic device. Here the ZnOnano particles, brought from Sigma-Aldrich, Germany are shown in Fig. 1 (b). ITO coated glass is used as front electrode whereas aluminium (Al) is used as the back electrode of the organic device.



(a) (b)

FIG. 1 Structure of (a) Crystal Violet dye and (b) Zinc Oxide (ZnO) nanoparticles

1 gm of PMMA and 5 ml of chlorobenzeneare mixed to form the solution of Poly methyl methacrylate (PMMA). PMMA is used as the inert binder to stick the dye solution on the electrodes. 1 mg of CV dye is added to the PMMA solution and stirred well for around 30 min.One part of this dye solution is separated in a beaker and 1 mg of ZnO nanoparticles are added to it and stirred well and is kept for several hours until all the substances are entirely dissolved to get the proper solution. After that the prepared solution is spin coated on both pre cleaned ITO coated glass and Al back electrode at a speed of 1500 rpm and then dried at a speed of 2500 rpm [8]. When the electrodes reach semi-dry state, they are sandwiched together to form the devices. The schematic diagram of the device is shown in Fig. 2.

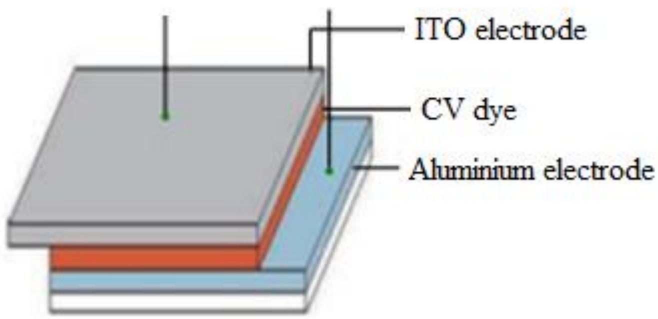


FIG. 2 Schematic diagram of sandwich type Crystal Violet dye based organic device

3. Measurements

Steady state current - voltage (I-V) characteristics of the devices have been measured with a Keithley 2400 source measure unit. For the I-V measurement of the device, the front electrode is connected to the positive terminal of the battery and the negative terminal of the battery is connected to back electrode of the device. The bias voltage is varied from 0 to 6 volt in steps of 0.5 volt with 1000 ms delay in our experiment. The experiments have been done in the clean open atmosphere of the laboratory at a temperature of 27°C.

4. Results and Discussions

Experimentally observed current–voltage (I-V) characteristics of these organic devices are compatible with thermionic emission theory. The current through a metal-organic semiconductor interface due to thermionic emission theory can be expressed as [9-13]

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1\right] \quad (1)$$

Where I_0 is the saturation current, which is given by:

$$I_0 = AA^* T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2)$$

and

$$A^* = \frac{4\pi q m^* k^2}{h^3} \quad (3)$$

Here, q is the electronic charge, V is the applied voltage, A is the area of the device, k is the Boltzmann's constant, T is the absolute temperature, A* is the effective Richardson constant of $120Am^{-2}K^{-2}$ for Crystal Violet dye, ϕ_b is the injection barrier height and n is the ideality factor.

The dark I-V characteristics of CV dye based organic device in absence and presence of ZnO nanoparticles are shown in Fig. 3. The value of dark current is quite low for the CV dye under experiment. But current increases when ZnOnanoparticles are incorporated with this CV dye based organic device.

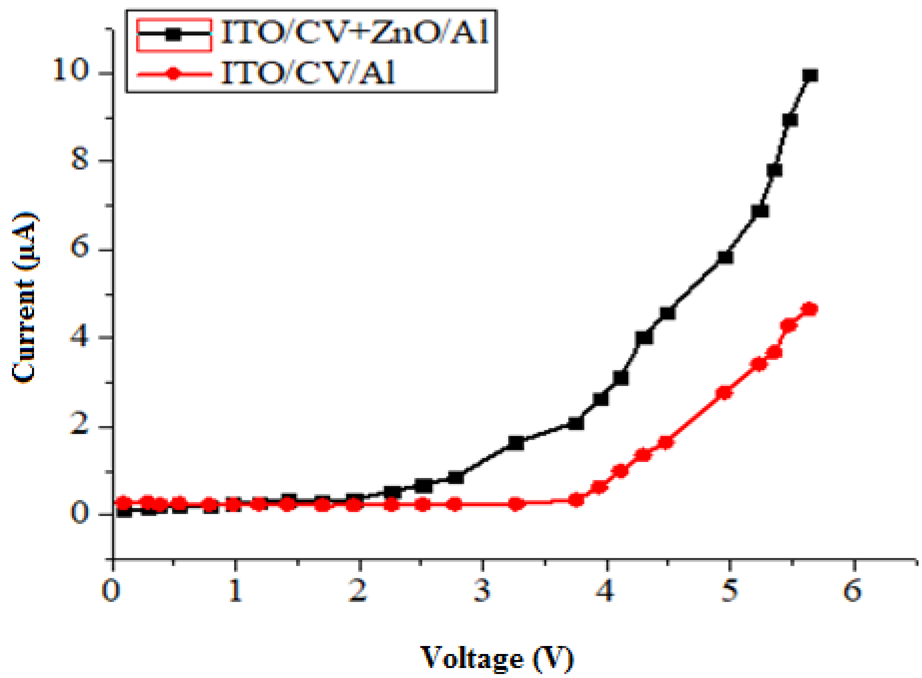


FIG. 3 Dark I-V characteristic of ITO/CV/Al based organic device in absence and presence of ZnO nanoparticles

Interfacial Barrier Height of metal - organic semiconductor device can be determined from the following relation [14-16]

$$\phi_b = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_0}\right) \quad (4)$$

Fig. 4 shows semi logarithmic I-V curves of CV dye based organic device in absence and presence of ZnO nanoparticles respectively. The reverse saturation current I_0 is determined from the y-intercept of both the semi logarithmic I-V curves. Applying equation (4), the barrier height of CV dye based organic device is calculated which is 0.87 eV in absence of ZnO nanoparticles and the value of barrier height reduces to 0.78 eV in presence of ZnO nanoparticles.

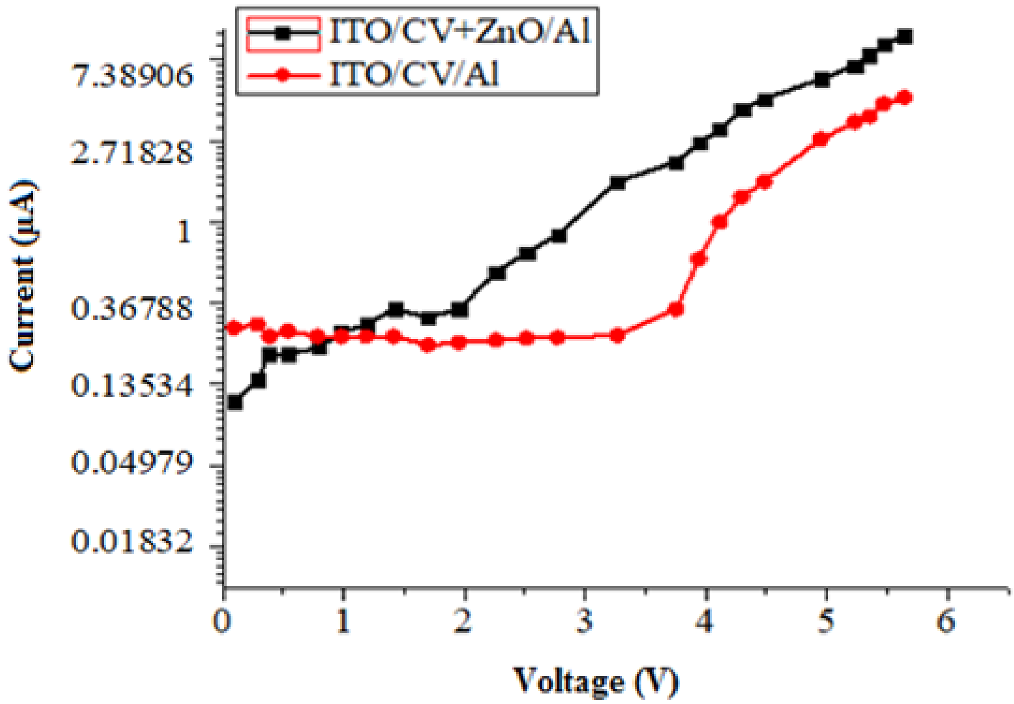


FIG. 4 Semi logarithmic plot of ITO/CV/Al based organic device in absence and presence of ZnO nanoparticles

The injection barrier height can also be calculated using Norde function. In this Norde function, the relationship between the function F (V) and the measured current I (V) can be expressed in the equation given below [17]. I (V) is the current, measured from I-V characteristics of the device.

$$F(V) = \left(\frac{V}{X}\right) - \frac{kT}{q}\ln\left(\frac{I(V)}{AA^{*}T^{2}}\right) \quad (5)$$

where X is the first integer greater than n. The value of current I (V_0) corresponding to minimum value of Norde's function F (V_0), where V_0 is the corresponding voltage.

In Fig. 5 for ITO/CV/Al structure and ITO/CV+ZnO/Al structure respectively, the barrier height has been calculated by using the following equation [18]. V_0 is estimated from the plot which is shown in Fig. 5.

$$\phi_b = F(V_0) + \frac{V_0}{X} - \frac{kT}{q} \quad (6)$$

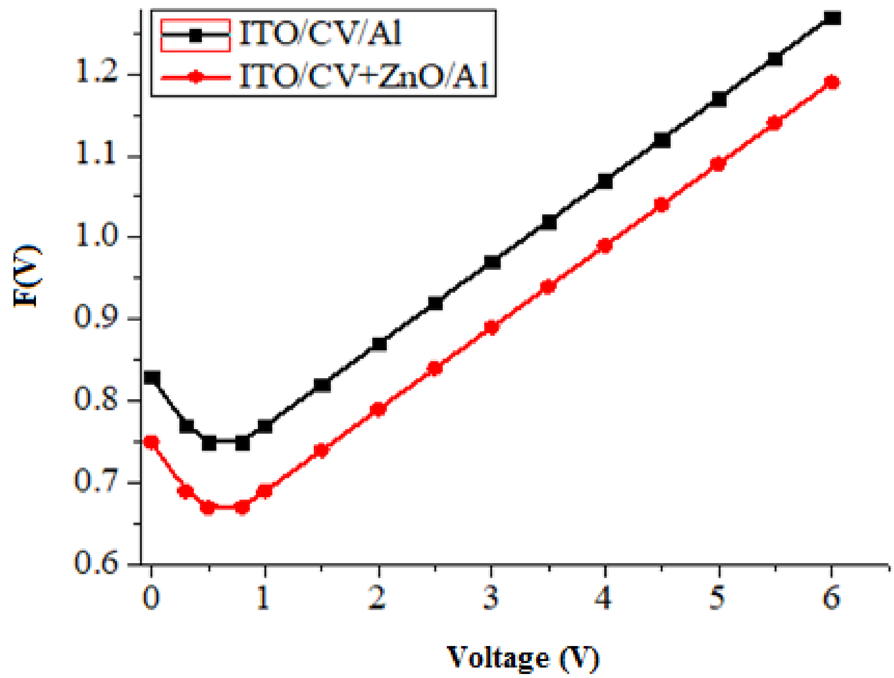


FIG. 5 Norde function F (V) – V plot of ITO/CV/Al based organic device in absence and presence of ZnO nanoparticles

The values of threshold voltage, barrier height of CV dye based organic devices in absence and presence of ZnOnanoparticles are shown in Table 1.

Table 1 The values of threshold voltage, barrier height of CV dye based organic devices in absence and presence of ZnOnanoparticles

Device	Threshold voltage (V)	Barrier height from I-V characteristics (eV)	Barrier height using Norde's Function (eV)
ITO/CV/Al	3.93	0.87	0.83
ITO/CV+ZnO nanoparticles/Al	3.00	0.78	0.77

5. Conclusions

In this paper, we have studied the injection barrier height of CV dye based organic device. Barrier height affects the charge injection process at the metal – organic layer interface. In this work, it has been seen that reduction of injection barrier height at the metal – organic layer interface significantly improves the current flow in thisCV dye based organic devices. By incorporating ZnO nanoparticles the barrier height has been reduced in this organic device.The higher electron mobility of zinc oxide nanoparticles facilitates efficient charge injection at the interface by reducing the barrier height. The barrier height in absence and presence of ZnO nanoparticles are calculated using the plot of I-V characteristics of these devices and also by using Norde method. Both the methods show a reduction of barrier height of 10.34 % and 7.22% respectively in presence of ZnO nanoparticles.Incorporation of ZnOnanoparticles also reduce the threshold voltage of the device from 3.93 V to 3V, which can be attributed to reduction of interfacial injection barrier. The improvement of charge flow in the organic device will also improve the conductivity of the organic device.

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REFERENCES

[1] M. Caironi, and Y.Y. Noh, Large Area and Flexible Electronics, Wiley –VCH(2015)

[2] U.Wolf, V. Arkhipov and H.Bässler, Physical Review B 59, 11 (1999)

[3]H. Tajima, K. Yoshida, S. Sato, T. Kadoya and J.I. Yamada, The Journal of Physical Chemistry C 121, 27 (2017)

[4] A.Kumatani, Y. Li, P. Darmawan, T.Minariand K.Tsukagoshi, Nature 3, 1026 (2013)

[5] J. Pan, J. Chen, Q. Huang, Q. Khan,X. Liu, Z. Tao, Z. Zhang,W. Lei and A. Nathan, ACS Photonics 3, 215 (2016)

[6] M.E. Aydın, T. Kılıçoğlu, K. Akkılıç, and H. Hoşgören, Physica B 381, 1(2006)

[7] R.C. Chen , K.J. Wei, T.M. Wang , Y.M. Yu , J.Y. Li , S.H. Lee, W.H. Wang , T.J. Ren, C.W. Tsai, Journal of Food and Drug Analysis 21, 4 (2013)

[8] S.Chakraborty, N.B.Manik, Physica B 481, 209 (2016)

[9] N. Armbrust, F. Schiller, J.Güdde and U. Höfer, Nature 7, 46561 (2017)

[10] S.M.Sze, K. K.Ng, Physics of Semiconductor Devices, John Wiley &Sóns, 3rd Ed., (2007)

[11] K. Chakraborty, S. Chakraborty and N. B. Manik, Journal of Semiconductor 39, 9 (2018)

[12] M. Shah,Kh.S.Karimov, Z. Ahmad and M.H. Sayyad, Chinese Physics Letter 27, 106102 (2010)

[13] Z. Harrabi, S. Jomni, L.Beji and A. Bouazizi, Physica B. 405, 3745 (2010)

[14] H.M. J. Al-Ta'ii , Y. M. Amin and V. Periasamy, Sensors 15, 3 (2015)

[15] M.Yildirim, Journal of Polytechnic 20, 1 (2017)

[16] B. Güzeldir., M.Sağlam, A. Ateş, and A.Türüt, Journal of Alloys and Compounds 627,200 (2015)

[17] H.Norde, Journal of Applied Physics 50, 5052 (1979)

[18] F.Yakuphnoglu, M. Shah, A. W. Farooq, ActaPhysicaPolonica A120, 558 (2011)