Effect of Carboxyl-Functionalized Single Walled Carbon Nanotubes on the Interfacial Barrier Height of Malachite Green Dye Based Organic Device

Sudipta Sen and Nabin Baran Manik

Department of Physics, Condensed Matter Physics Research Centre, Jadavpur University, Kolkata-700032, India

Article history
Received: 13-04-2019
Revised: 01-07-2019
Accepted: 29-07-2019

Abstract: In this study, we have estimated the interfacial barrier height ($\phi_b$) of Indium Tin Oxide (ITO) coated glass/Malachite Green (MG) dye/Aluminium (Al) based organic device and subsequently we have also observed the effect of carboxylfunctionalized SWCNT (COOH-SWCNT) on the $\phi_b$. Presence of COOH-SWCNT reduces the interfacial barrier height as SWCNT acts as filler and provides easy path for charge percolation. We have used ITO coated glass and aluminium as front electrode and back electrode respectively to form the organic device. This organic device has been prepared with and without COOH-SWCNT by using spin coating technique. We have measured the steady state current-Voltage (I-V) characteristics of the device to estimate the interfacial barrier height ($\phi_b$) of the device. $\phi_b$ is reduced from 0.67 eV to 0.59 eV in the presence of COOH-SWCNT. We have also estimated the $\phi_b$ by using Norde’s Method. This method also shows a reduction of interfacial barrier height from 0.72 eV to 0.64 eV due to incorporation of COOH-SWCNT. Both the methods show good consistency with each other. Reduction of the interfacial barrier height in presence of COOH-SWCNT indicates the enhancement of charge injection through the metal-organic dye interface. By suitable doping or addition of COOH-SWCNT within the MG dye it is possible to reduce the barrier height and enhance the current injection through metal-organic dye interface.

Keywords: Interfacial Barrier Height, Malachite Green Dye, Metal-Organic Dye Interface, COOH-SWCNT

Introduction

Organic/Polymeric materials are being widely studied to develop different electronic/optoelectronic devices. These devices provide flexibility, cost effectiveness and can be easily fabricated over a large area (Kim et al., 2011; Tessler et al., 2009). Despite these advantages, there are also certain limitations of organic devices. One of the major limitations is when a metalorganic contact is formed; the charge injection is poor due to presence of high barrier height ($\phi_b$) at metal organic layer interface. There is not much study on the barrier height at the metal-organic layer interface. Attempts need to be made to reduce the interfacial barrier height in order to improve the charge injection at the interface of metalorganic layer. The injection of charges at the metal-organic layer interface has significant influence on the electrical properties of these organic devices and creates more impact than charge transport within the organic devices. The charge injection barrier at the interface between a metal and organic material is commonly described by the interfacial barrier of metal to semiconductor contact (Kumatani et al., 2013). Basically the interfacial barrier height is caused by the difference between the fermi energy level of metal and the energy band of organic material.

To reduce the barrier height at the metal-organic layer interface, we have incorporated COOH-SWCNT within the device. Presence of COOH-SWCNT decreases the barrier height at the metal-organic semiconductor interface as the high aspect ratio of COOH-SWCNT allows efficient conduction pathways for the generated charge carriers (Chakraborty and Manik, 2014). Generally, functionalized CNTs have certain advantages over their non-functionalized form. In comparison to non-functionalized forms functionalized SWCNTs have better interfacial bonding.
strength and form better dispersions in solvents. It is possible that functionalized groups may be attached either to the ends or to side chain of the main tube to form a branch like structure (Luo et al., 2012; Aqel et al., 2012).

Reduction of interfacial barrier height will lead to better injection of charges at the interface and thus will provide better conductivity. Injection current usually consists of thermionic-injection current and field-induced tunneling current. In the case of low voltages, tunneling injection is negligible and thermionic emission dominates (Bullejos et al., 2008). In this study, we have used Richardson-Schottky (RS) model of thermionic emission to characterize the organic device (De and Olawole, 2019).

Materials and Sample Preparation

Malachite Green (MG) is a cationic dye with the chemical formula $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$. The structure of the dye is shown in Fig. 1a. It belongs to the triaryl methane group and has a molar mass of 364.911 g/mol (chloride). The chloride and oxalate anions have no effect on the color. On a larger scale it is prepared by condensation of 2 moles of dimethylaniline with one mole of benzaldehyde at 100°C in presence of zinc chloride or concentrated sulphuric acid (Raducan et al., 2008). The cationic form of this dye has an extended pi-delocalization which allows absorbance of light in the visible range. The quantum yield of MG dye is quite high (Bongsup et al., 2003).

In our present work, MG dye and COOH-SWCNT are purchased from Finar Chemicals, Ahmedabad and Cisco Research Laboratories, India respectively. Figure 1(a) and 1(b) show the structures of MG dye and COOH-SWCNT respectively. Poly Methyl Methacrylate (PMMA) and Dichloromethane (DCM) solvent are purchased from Sigma Aldrich and Merck Specialities Pvt. Ltd, Mumbai respectively. It has been selected as a solvent in our work due to its high ability to dissolve organic compounds (Shuugrue et al., 2015). Figure 1(c) shows the structure of Dichloromethane (DCM).

Two different types of cells are prepared in order to observe the effect of COOH-SWCNT on MG dye based organic device, one type of cell is prepared with only MG dye and the other type of cell is prepared by adding COOH-SWCNT with this dye. To prepare the MG solution, 10 ml of DCM is taken in a clean test tube and in it 1g of PMMA is added. In this work, PMMA acts as an inert binder. The mixture is stirred with a magnetic stirrer for 30 min to get a clear solution. In this solution, 1 mg of MG dye is added and stirred for 15 min. This solution is then divided into two parts in two pre-cleaned test tubes. One test tube is kept aside and in the other 1 mg of COOH-SWCNT is added and stirred for 2 hours to get a homogeneous dispersed solution of dye and COOH-SWCNT.

To prepare the device, the MG solution is taken and coated on a pre-cleaned ITO coated glass. The film is coated on a spin coater at a speed of 1500 rpm and dried at a speed of 3500 rpm. The same solution is spin coated on the Al counter electrode. Both these electrodes are sandwiched together to form the MG dye cell. In a similar manner, another cell is prepared where COOH-SWCNT is added with MG dye. All the cells are kept in vacuum for 12 hours to dry before using them for characterization. The schematic diagram of the organic device is shown in the Fig. 2.

![Fig. 1: Structural diagram of (a) Malachite Green (MG) (b) COOH functionalized single walled carbon nanotubes (COOH-SWCNT) and (c) structure of Dichloromethane (DCM)](image-url)
Fig. 2: Schematic diagram of the device. ITO coated glass is used as the front electrode and Al is used as the back electrode and MG dye is used as an active layer

Measurements

Dark current-Voltage (I-V) characteristics of the cells have been measured with a Keithley 2400 source measure unit. For dark I-V measurement, 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. During measurement, the bias voltage is varied from 0 to 6 volt in steps of 0.5 volt with 1500 MS delay. The experiments have been done in the clean open atmosphere of the laboratory at a room temperature of 25°C.

Results and Discussion

The current through a metal-organic semiconductor interface due to thermionic emission can be expressed as (Sze and Kwok, 2007; Chakraborty et al., 2018; Shah et al., 2010a; Yakuphanoglu, 2010; Aydin et al., 2006):

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

(1)

where, \( I_0 \) is the saturation current, which is given by:

\[ I_0 = A^* T^2 \exp \left( \frac{-\phi_b}{kT} \right) \]  

(2)

and:

\[ A^* = \frac{4\pi qn^* k^2}{h^3} \]  

(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 120 Am⁻²K⁻² for Malachite Green dye, \( \phi_b \) is the interfacial barrier height and \( n \) is the ideality factor.

The dark I-V characteristics of MG dye based organic device in absence and presence of COOH-SWCNT are shown in Fig. 3(a) and 3(b) respectively. The value of dark current is quite low for the MG dye under experiment. But current becomes double when COOH-SWCNTs are incorporated with this MG dye based organic device.

Interfacial Barrier Height of metal-organic semiconductor device can be determined from the following relation (Al-Ta’ii et al., 2015; Shah et al., 2010b; Harrabi et al., 2010):

\[ \phi_b = \frac{kT}{q} \ln \left( \frac{A^* T^2}{I_0} \right) \]  

(4)

Figure 4(a) and 4(b) show semi logarithmic I-V curves of MG dye based organic device in absence and presence of COOH-SWCNT 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 MG dye based organic device is calculated which is 0.67 eV in absence of COOH-SWCNT and the value of barrier height reduces to 0.59 eV in the presence of COOH-SWCNT.

The interfacial barrier height can also be calculated using Nordé’s function. In this Nordé’s function, the relationship between the function \( F(V) \) and the measured current \( I(V) \) can be expressed in the equation given below (Norde, 1979). \( I(V) \) is the current, measured from I-V characteristics of the device

\[ F(V) = \frac{V}{X} - \frac{kT}{q} \ln \left( \frac{I(V)}{A^* T^2} \right) \]  

(5)

where, \( X \) is the first integer greater than \( n \). The value of current \( I(V_0) \) corresponding to minimum value of Nordé’s function \( F(V_0) \), where \( V_0 \) is the corresponding voltage (Yakuphanoğlu et al., 2011).

Figure 5(a), for ITO/MG/Al structure, the interfacial barrier height has been calculated by using the following equation (Kocyigit et al., 2019). \( V_0 \) is estimated from the plot which is shown in Fig. 5(a):

\[ \phi_b = F(V_0) + \frac{V_0}{X} - \frac{kT}{q} \]  

(6)

To compare the effect of COOH-SWCNT, we have plotted the Nordé’s function in Fig. 5(b), by using the Equation (5). Consequently, the interfacial barrier height has been calculated for ITO/MG+COOH-SWCNT/Al structure by using the Equation (6).
The values of barrier height of MG dye based organic devices in absence and presence of COOH-SWCNT has been shown in Table 1.

From Table 1, it can be seen that both the methods show the reduction of barrier height as 11.94% and 11.11% respectively in the presence of COOH-SWCNT. It can be said that by incorporating COOH-SWCNT, reduction of barrier height help in improving better current injection so that the organic device can be turned on at much lower voltage.

![Graph (a)](image1)

![Graph (b)](image2)

**Fig. 3:** Dark I-V characteristics of organic device comprising of MG dye (a) without COOH-SWCNT and (b) with COOH-SWCNT
Fig. 4: In I-V characteristics of organic device comprising of MG dye (a) without COOH-SWCNT and (b) with COOH-SWCNT

Fig. 5: Norde’s function F(V)-V plot of (a) ITO/MG/Al structure and (b) ITO/MG+COOH-SWCNT/Al structure
**Table 1:** Calculation of barrier height of MG dye based organic devices in absence and presence of COOH-SWCNT

| Dye under consideration | Barrier height from I-V characteristics (eV) | Barrier height using Norde’s function (eV) |
|-------------------------|-----------------------------------------------|------------------------------------------|
| MG                      | 0.67                                          | 0.72                                     |
| MG+COOH-SWCNT           | 0.59                                          | 0.64                                     |

**Conclusion**

In this study, we have studied the effect of COOH-SWCNT on the interfacial barrier height of MG dye based organic device. Values of barrier height for MG dye based organic device are calculated by analyzing I-V characteristics of the device and also by Norde’s function. Both the methods show good consistency with each other. It is observed that in presence of COOH functionalized single walled carbon nanotube, the barrier height at the metal-organic layer interface is reduced. Reduction of interfacial barrier height improves the charge injection which results in higher conductivity.

**Acknowledgement**

The author sincerely acknowledges University Grants Commission (UGC), India for financial assistance and one of the authors, Sudipta Sen is thankful to UGC for awarding a research fellowship.

**Data Availability**

Data used to support the findings of this study are included within this article.

**Author’s Contributions**

**Sudipta Sen:** Participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

**Nabin Baran Manik:** Designed the research plan and organized the study.

**Conflicts of Interest**

The authors declare that there is no conflict of interest.

**References**

Kim, J.J., M.K. Han and Y.Y. Noh, 2011. Flexible OLEDs and organic electronics. Semicond. Sci. Technol.

Tessler, N., Y. Preezant, N. Rappaport and Y. Roichman, 2009. Charge transport in disordered organic materials and its relevance to thin-film devices: A tutorial review. Adv. Mater, 21: 2741-2761. DOI: 10.1002/adma.200803541

Kumatani, A., Y. Li, P. Darmawan, T. Minari and K. Tsukagoshi, 2013. On practical charge injection at the metal/organic semiconductor interface. Nature, 3: 1026-1026. DOI: 10.1038/srep01026

Chakraborty, S. and N.B. Manik, 2014. Effect of COOH-functionalized SWCNT addition on the electrical and photovoltaic characteristics of Malachite Green dye based photovoltaic cells. J. Semicond.

Luo, Y. Z. Gong, M. He, X. Wang, Z. Tang and H. Chen, 2012. Fabrication of high-quality carbon nanotube fibers for optoelectronic applications. Solar Energy Mater. Solar Cells, 97:78-82. DOI: 10.1016/j.solmat.2011.09.036

Aqel, A., M.M. Kholoud, A. El-Nour, R.A.A. Ammar and A. Al-Warthan, 2012. Carbon nanotubes, science and technology part (I) structure, synthesis and characterisation. Arabian J. Chem., 5: 1-23. DOI: 10.1016/j.arabjc.2010.08.022

Bullejos, P.L., J.A.J. Tejada, M.J. Deen, O. Marinov and W.R. Datars, 2008. Unified model for the injection and transport of charge in organic diodes. J. Applied Phys., 103: 064504-064504. DOI: 10.1063/1.2884711

De, D.K. and O.C. Olawole, 2019. A three-dimensional model for thermionic emission from graphene and carbon nanotube. J. Phys. Commun.

Raducan, A., A. Olteanu, M. Puiu and D. Oancea, 2008. Influence of surfactants on the fading of malachite green. Formerly Central European J. Chem., 6: 2391-5420. DOI: 10.2478/s11532-007-0066-0

Bongsup, P.C., T. Yang, L.R. Blankenship, J.D. Moody and M. Churchwell et al., 2003. Synthesis and characterization of N-demethylated metabolites of malachite green and leucomalachite green. Chem. Res. Toxicol, 16: 285-294. DOI: 10.1021/tx0256679

Shuugrue, C.R. H.H. Mentzen and B.R. Linton, 2015. A colorful solubility exercise for organic chemistry. J. Chem. Educ., 92: 135-138. DOI: 10.1021/ed4005408

Sze, S.M. and K.N.G. Kwok, 2007. Physics of Semiconductor Devices. 3rd Edn., Wiley and Sóns, ISBN-13: 978-0-471-14323-9, pp: 832.

Chakraborty, K., S. Chakraborty and N.B. Manik, 2018. Effect of single walled carbon nanotubes on series resistance of rose bengal and methyl red dye-based organic photovoltaic device. J. Semicond., 39:094001-094001. DOI: 10.1088/1674-4926/39/9/094001

Shah, M., K.S. Karimov, Z. Ahmad and M.H. Sayyad, 2010a. Electrical characteristics of Al/CNT/NiPc/PePC/Ag surface-type cell. Chinese Phys. Lett., 27: 106102-106102. DOI: 10.1088/0256-307X/27/10/106102
Yakuphanoglu, F., 2010. Controlling of silicon–insulator–metal junction by organic semiconductor polymer thin film. Synth. Metals, 160: 1551-1555. DOI: 10.1016/j.synthmet.2010.05.024

Aydın, M.E. T. Kılıçoğlu, K. Akkılıç and H. Hosğoren, 2006. The calculation of electronic parameters of an Au/β-carotene/n-Si Schottky barrier diode. Physica, 381: 113-117. DOI: 10.1016/j.physb.2005.12.254

Al-Ta’ii, H.M.J., Y.M. Amin and V. Periasamy, 2015. Calculation of the electronic parameters of an Al/DNA/p-Si schottky barrier diode influenced by alpha radiation. Sensors, 15: 4810-4822. DOI: 10.3390/s150304810

Shah, M., M.H. Sayyad, K.S. Karimov and F. Wahab, 2010b. Electrical characterization of the ITO/NiPc/PEDOT: PSS junction diode. J. Phys. Applied Phys.

Harrabi, Z., S. Jomni, L. Beji and A. Bouazizi, 2010. Distribution of barrier heights in Au/porous GaAs schottky diodes from current-voltage-temperature measurements. Physica B: Condensed Matter, 405: 3745-3750. DOI: 10.1016/j.physb.2010.05.079

Norde, H., 1979. A modified forward I-V plot for Schottky diodes with high series resistance. J. Applied Physics, 50: 5052-5053. DOI: 10.1063/1.325607

Yakuphnoglu, F., M. Shah and A.W. Farooq, 2011. Electrical and interfacial properties of p-Si/P3HT organic-on-inorganic junction barrier. Acta Phys. Polonica, 120: 58-562.

Kocyigit, A., M. Yılmaz, S. Aydogan and Ü. İncekara, 2019. The effect of measurements and layer coating homogeneity of AB on the Al/AB/p-Si devices. J. Alloys Compounds, 790: 388-396. DOI: 10.1016/j.jallcom.2019.03.179