Journal of Basic and Applied Engineering Research
Print ISSN: 2350-0077; Online ISSN: 2350-0255; Volume 1, Number 4; October, 2014 pp. 85-89

http://www.krishisanskriti.org/jbaer.html

Size Effect of Multi-walled Carbon Nanotubes on the Performance of Malachite Green Dye Based Photovoltaic Devices

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Abstract: **In this work we report on the photovoltaic effects of three different sizes of multi-walled carbon nanotubes (MWCNTs) on malachite green (MG) dye based photovoltaic devices. Photovoltaic devices were prepared by sandwiching a thin layer of MG dye in between ITO and Al-Mylar electrodes. In these devices, three different sizes of MWCNTs, namely of 8 nm, 30 nm and 50 nm are incorporated separately. The devices are characterized through different electrical and photovoltaic measurements. From the dark I-V characteristics the transition voltage for the different devices are measured and it is observed that for 8 nm MWCNT device, the transition voltage is lowest. Experimental data reveal that the photovoltaic response is higher in case of 8 nm MWCNT compared to 30 nm and 50 nm MWCNTs. Photovoltaic parameters such as open circuit voltage, short circuit current and fill factor are also found to increase for 8 nm MWCNT. Incorporation of carbon nanotubes in the photoactive layer provides additional paths for the electrons through the carbon nanotubes percolation network. This reduces the charge recombination and enhances electron conduction through the system. It is expected that 8 nm MWCNT shows higher performance than 20-30 nm and 50 nm MWCNTs due to its better arrangement within the system. Longer sizes MWCNTs will easily align parallel to each other and pack into crystalline ropes due to strong inter-tube van der Walls attraction. This will reduce the conduction of electrons as the charges would get trapped in the nanotubes cluster thereby lowering the performance of the devices.**

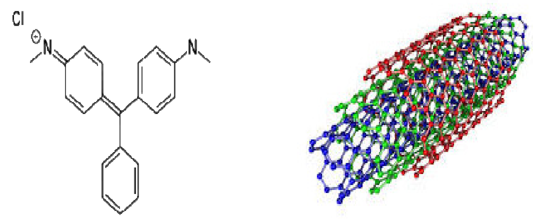
Keywords: **Malachite Green dye, MWCNT, photovoltaic response, charge recombination**

1. INTRODUCTION

Organic photovoltaic cells have attracted the attention due to their ease of fabrication, flexibility [1, 2]. But at the same time it should be mentioned that the efficiency of the OPV devices are quite low [3] as compared to the silicon based devices. Different techniques such as modification of electrodes, structure of the devices, addition of new materials are being employed for increasing the efficiency of these devices. Recently, for enhancing the performance of these OPV devices, researchers are incorporating different nanoparticles [4,5], carbon nanotubes [6] into these devices. Different literatures have shown that incorporation of multi-walled carbon nanotubes (MWCNTs) increases the device performance [7, 8]. MWCNTs are basically a bundle of concentric single-walled carbon nanotubes (SWCNTs) with different diameters. They have an interlayer distance of the order of the distance between graphene layers in graphite. It is believed that MWCNTs form percolated networks which help in better charge transport.

They act as excellent charge acceptors which enhances the movement of charges through the system. There are reports showing the use of MWCNTs in different dye sensitized solar cells [9, 10]. In 2005 GE Global Research observed a photovoltaic effect in a pristine nanotube diode device consisting of two CNTs with different electrical properties. But much work is not done on studying the effect of different sizes of these MWCNTs on the electrical and photovoltaic characteristics of organic dye based photovoltaic devices. Variation in sizes of these incorporated MWCNTs can cause lot of changes in the performance of the OPV devices. So the study of these characteristics is of much interest.

In this regard in our present work we have studied the effect of different sizes of MWCNTs on the electrical and photovoltaic characteristics of Malachite Green (MG) dye based photovoltaic devices. Three different sizes of MWCNTs namely 8 nm, 30 nm and 50 nm have been used in our study. MG is a cationic dye of the triarylmethane group. Using spin coating method, different cells are prepared by sandwiching a thin layer of MG between Indium Titanium Oxide(ITO) and Aluminum coated on Mylar sheet(Al-M). Here ITO is used as the front electrode and Al-M is used as the back electrode. Our earlier works show that Al-M reports better performance [11] than ordinary Al as back electrode due to its high reflectivity. In these cells MWCNTs of 8 nm, 30 nm and 50 nm are separately incorporated.



(a) **(b)**

Fig. 1. Structure of (a) Malachite Green (MG) dye and (b) Multi-walled carbon nanotubes (MWCNT)

The cells fabricated are characterized by different electrical and photovoltaic measurements and the results analysed. Fig. 1 (a) and 1 (b) show the structure of MG dye and MWCNT respectively.

2. EXPERIMENTAL DETAILS

MG dye and MWCNTs are purchased from Finar Chemicals, Ahmedabad and Sisco Research Laboratories, India respectively. PolyMethyl Methacrylate (PMMA) is procured from Merck Specialities Pvt. Ltd, Mumbai. Here PMMA acts as an inert binder.

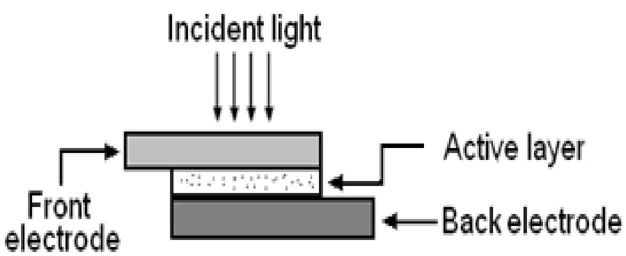


Fig.2. Schematic diagram of an organic photovoltaic cell. ITO coated glass is used the front electrode and a thin layer of Aluminium (Al) coated on a Mylar sheet is used as the back electrode. The active layer containing the dye solution is sandwiched between the two electrodes.

To prepare the MG dye solution, 10 ml of double distilled water is taken in a clean test tube and in it 1g of PMMA is added. The mixture is stirred with a magnetic stirrer for 30 min to get a clear solution. In this solution, 1mg of MG dye is added and stirred for 15 min. This solution is then divided into three parts in three pre-cleaned test tubes. In the first, second and third test-tubes MWCNT of size 8 nm, 30 nm and 50 nm are added respectively and stirred for 2 hours to get a homogeneous dispersed solution of dye and MWCNT. These solutions are used to prepare different devices in a similar manner. The cells prepared by respectively adding 8 nm, 30 nm and 50 nm MWCNT with MG dye are termed as Cell-1, Cell-2 and Cell-3 respectively.

3. MEASUREMENTS

The dark current-voltage (I-V) characteristics of the two different cells have been measured with a Keithley 2400 source measure unit. During measurement, the bias voltage is varied from 0 to 6 volts in steps of 0.5 volts with 1500 ms delay. Pulsed photocurrent measurement is done with Agilent data-logger (Model 34970A) data acquisition system. A solar simulator (Model 150 W Newport Corporation) has been used as the light source for the photovoltaic measurement. Fig.4 shows the schematic diagram of the experimental set-up for photovoltaic measurement. The photocurrent and photo voltage are measured with a digital current nanometer and Keithley 2000 multimeter respectively. The experiments are performed in the clean open atmosphere of the laboratory where temperature was 22^0C.

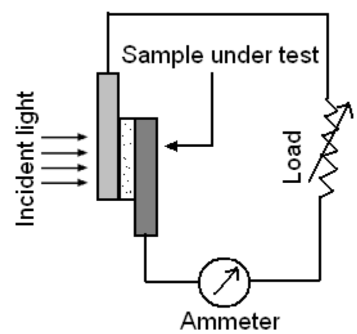


Fig. 4. Experimental set-up for photovoltaic measurement. Light is incident on the ITO caoted glass. Two leads are connected from the electrodes across the load resistance which completes the circuit.

4. DISCUSSION & RESULTS

Figure 6 shows the dark I-V characteristics of Cell-1, Cell-2 and Cell-3 respectively. From the figures it is observed that the dark current of the cells have two distinct regions. Observations show that beyond a certain transition voltage (V_{th}), the current conduction mechanism changes for all the cells. This V_{th} is minimum for Cell-1. To have a better insight of the conduction mechanism, we consider an exponential distribution of trap states for our system and solve the Poisson equation. The exponentially distributed trap charge concentration (n_t) may be expressed as

$$n_t = H_n \exp\left(\frac{F_n}{kT_c}\right) \quad (1)$$

where H_n is the trap density, F_n is the electron Fermi energy, k is Boltzmann constant, and T_c is characteristic temperature of the exponential trap distribution (i.e., $T_c = E_c/k$, where E_c is the characteristic trap energy). Solving the Poisson equation with this form of trap distribution, the I-V characteristic is calculated and found to be of the form [13,14]

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

where N_c is the effective density of states, μ is the mobility of charge carrier, L is the thickness, ε is equal to $\varepsilon_0\varepsilon_r$ with ε_0 being the permittivity of vacuum and ε_r the dielectric constant, V is the applied voltage and m = T_c/T, T_c is a "characteristic temperature" that describes the trap distribution in the system and m is a constant. The most notable feature of this equation is J~V $^{m+1}$. The log J versus log V plot gives a liner relationship and from the slope the value of (m+1) is obtained. Table 1 shows the values of the different parameters extracted form the dark I-V characteristics curves.

Table-1: Extracted values from ln I-ln V curves

Size of MWCNT used with MG dye (nm)	Threshold voltage V_{th} (volts)	m+1 (below V_{th})	m+1 (above V_{th})
8	2.37	1.13	3.03
30	2.71	1.17	3.47
50	2.83	1.24	3.94

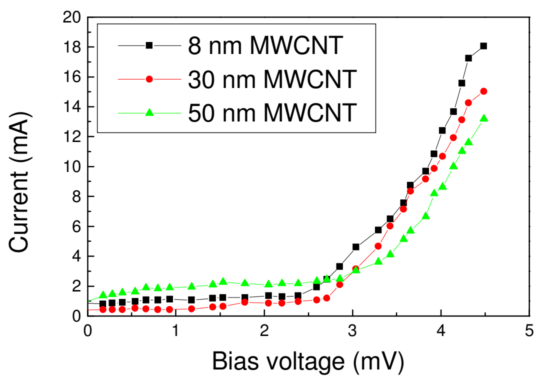


Fig.6. Dark current–voltage curves of the different cells

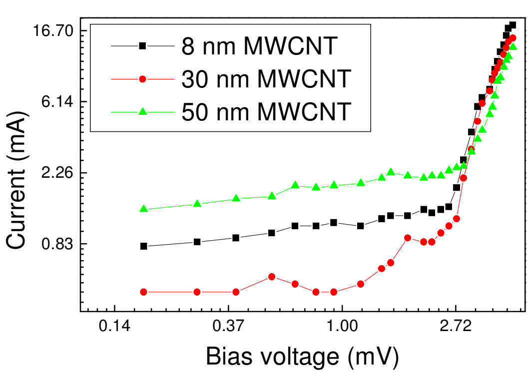


Fig.7. ln I-lnV characteristics of the cells

The power conversion efficiency (η) of the cells has been calculated using the equation

$$\eta\% = \frac{J_{sc} X V_{oc} X FF}{\Phi_0} X\, 100 \qquad (3)$$

where Φ_0 is the incident intensity of light and Fill Factor (FF) is defined by the relation

$$FF = \frac{V_m X J_m}{V_{oc} X J_{sc}} \qquad (4)$$

where V_m and J_m represent the voltage and current density for maximum power rectangle.

Fig. 8 (a), 8 (b) and 8 (c) show the photovoltaic measurements of Cell-1, Cell-2 and Cell-3 respectively. From the curves different photovoltaic parameters such as V_{oc}, I_{sc}, FF and power conversion efficiency are extracted and listed in Table 2.

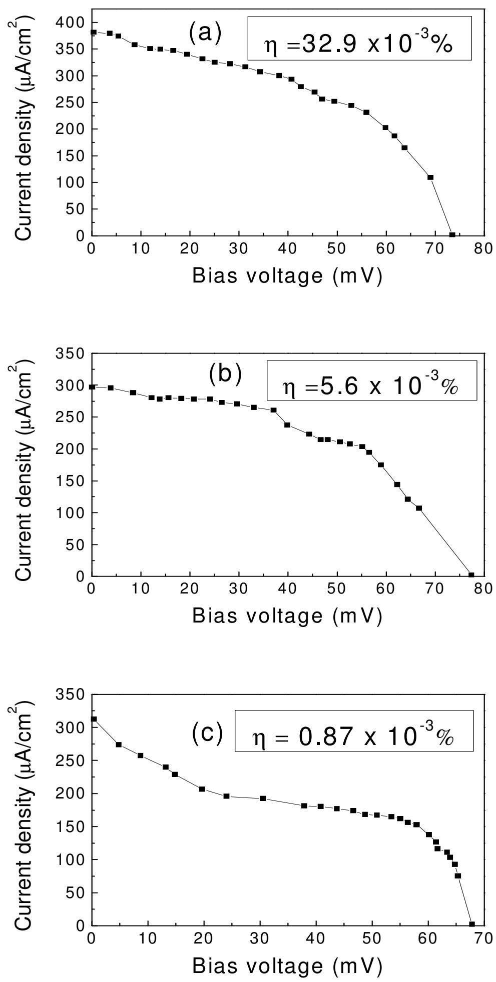


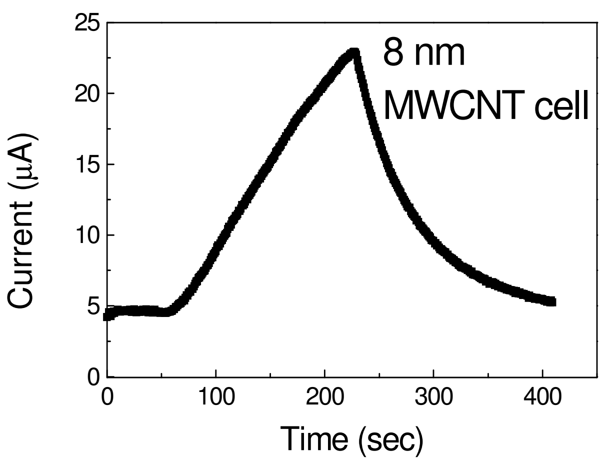
Fig. 8. Light I-V curves for (a) 8 nm, (b) 30 nm, (c) 50 nm MWCNT incorporated MG dye based OPV cell

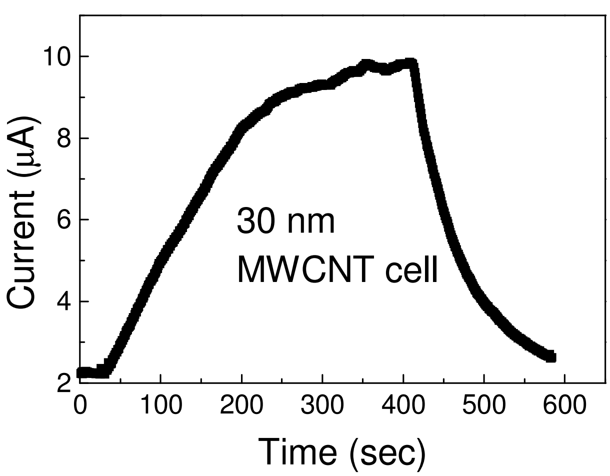
Table -2: Extraction of different photovoltaic parameters

Cell Name	Size of MWCNT used with MG dye (nm)	Voc (mV)	Jsc ($\mu A/cm^2$)	FF	η ($x10^{-3}$) %
Cell-1	8	74	381	0.458	32.9
Cell-2	30	78	298	0.376	5.6
Cell-3	50	67	301	0.265	0.87

From Table-2 it is observed that both the short circuit current density and the power conversion efficiency are much higher for the MG dye cell where 8 nm MWCNT has been added.

To further see the effect of MWCNT on the charge separation and relaxation dynamics of the cells, we performed photo-response measurements of the cell under an pulsed optical radiation of $100mW/cm^2$.





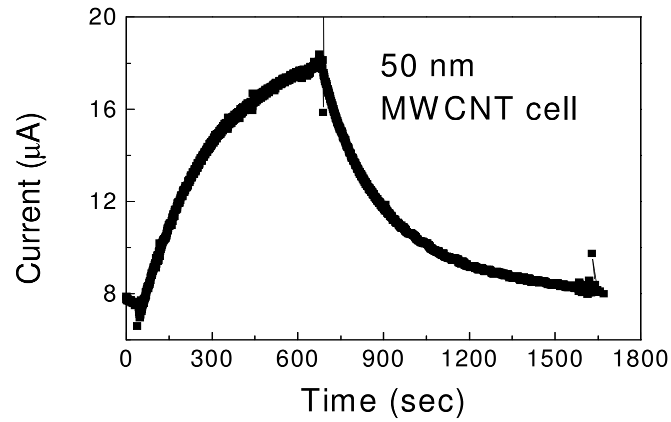


Fig. 9: Pulsed photo-response of (a) 8 nm, (b) 30 nm and (c) 50 nm MWCNT added MG dye based cell

For an optical pulse a square shaped photocurrent is expected. Any deviation from this indicates that the complete charge relaxation process is hampered. Sharp increase and decrease in photocurrent indicates that the charge separation is fast and charge recombination is reduced. Fig.9 (a), 9(b) and 9(c) show the pulsed photo-response of the cells.

From the above figure it is observed that in comparison to the other two cells the current is much higher for the 8 nm MWCNT added MG dye based photovoltaic cell. Also the growth and decay of photocurrent are quite faster for this cell. It is expected that due to their smaller size the 8 nm MWCNT help better in better charge separation and relaxation process which enhances the charge transport mechanism. The longer sizes MWCNTs may align parallel to each other and get bundled in ropes. This would result in increase of charge recombination and result in trapping of charge carriers. Our results also show that the power conversion efficiency of the 8 nm MWCNT cell is almost 30 times higher than the other two cells.

5. CONCLUSION

In this work the effect of different sizes of MWCNTs on the electrical and photovoltaic properties of MG dye based photovoltaic cells have been studied. Experimental data reveals that the device performance of the 30 nm and 50 nm MWCNT cells are found to be poor in comparison to the 8 nm MWCNT cell. Power conversion efficiency is almost 30 times for the 8nm MWCNT based MG dye cell. From the pulsed photocurrent measurement result it is observed that the photocurrent is quite high for the 8 nm MWCNT cell. It is expected that due to their smaller sizes 8 nm MWCNTs enhance the charge separation and relaxation process. This reduces the charge recombination and enhances current conduction through the system. It is expected that due to their longer sizes these MWCNTs get aligned parallel to each other and form crystalline ropes. This would result in increase of charge recombination and affect the performance of the cells. Further investigation is needed in this regard.

6. ACKNOWLEDGEMENT

The authors thank University Grants Commission (UGC), India and Council of Scientific and Industrial Research (CSIR), India for providing the required financial assistance for supporting the project.

REFERENCES

[1] Zhiyong Liu,Dawei He, Yongsheng Wang, Hongpeng Wu,Jigang Wang, Haiteng Wang, Solar Energy Materials & Solar Cells 94 (2010) 2148–2153

[2] Jun H Gwang, Jin H Sung, Park H Sung, et al, Carbon 50 (2012) 40-46

[3] Yujie Yuan, Guofu Hou, Jianjun Zhang, et al. J. Semicond, 2009, 30 (3): 0340071-0340075

[4] Saha S, Manik N. B. Indian J Phys, July 2012, 86 (7): 605-611

[5] Lee Donggu, Bae Ki Wan, Park Insun, et al. Solar Energy Materials & Solar Cells, 2011, 95: 365-368

[6] Wang Shi-Hao, Hsiao Yu-Jen, Fang Te-Hua, et al. ECS Journal of Solid State Science and Technology, 2013, 2 (11): M52-M55

[7] Khatri Ishwor, Adhikari Sudip, Aryal Hare Ram, et al. Applied Phys Lett., 2009,94, 093509

[8] Liu Zhiyong, He Dawei, Wang Yongsheng, et al. Solar Energy Materials & Solar Cells,2010, 94:2148–2153

[9] Sreekala et al. Journal Of Nanostructure in Chemistry 2013, 3:19

[10] Ebrahim Shaker, Soliman Moataz et al. Int J. Photoenergy, 2013, doi.org/10.1155/2013/906820

[11] Haldar Ajanta, Maity Subhasis, Manik N. B., Ionics (2008) 14:263–267

[12] Chakraborty S, Manik N. B, Effect of COOH-functionalized SWCNT addition on the electrical and photovoltaic characteristics of Malachite Green dye based photovoltaic cells Journal of Semiconductors (2014), Accepted for publication

[13] Emmanuel Kymakis1, Nikolaos Kornilios and Emmanuel Koudoumas J. Phys. D: Appl. Phys. 41 (2008) 165110 (5pp)

[14] Islam Md. R., Maity S, Haldar A , Manik N. B , Basu A. N, Ionics (2012) 18:209–214