**Impact of MWCNT on Metal – Organic Contact of Rose Bengal and Safranin –T Dye Based Organic Device**

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**Abstract:**

Carbon-based nanomaterials (CBN) have gained significant attention in various research disciplines due to their exceptional characteristics, including an excellent aspect ratio, substantial surface area, and superior thermal and electrical conductivity. In this study, Multi walled carbon nanotubes (MWCNT) have been selected from an array of carbon-based nanomaterials. This study focuses on exploring the use of MWCNT within the realm of organic electronics. Organic dye-based devices possess distinct advantages in comparison to their inorganic counterparts, a fact well acknowledged in the field. However, there exist certain drawbacks associated with the utilization of organic dyes in the context of being positioned between two metallic electrodes, hence establishing metal-organic interface. The charge injection process during formation of metal-organic junction is influenced by the presence of a high concentration of traps and a high injection barrier at the contact region. The improvement in charge flow at the junction and the enhancement of conductivity, as well as the reduction in threshold voltage, can be achieved by decreasing these values. From this standpoint, the inclusion of MWCNT has been implemented within the device. In the process of fabricating organic dye-based devices, two distinct organic dyes, namely Rose Bengal (RB) dye and Safranin - T dye, have been selected. Four devices were developed, with two devices being made without the inclusion of MWCNT, while the other two devices incorporate MWCNT. This study aims to examine the impact of trap energy and injection barrier on the movement of charge carriers at the interface between metal and organic materials. Additionally, it seeks to investigate any alterations in these parameters when MWCNTs are present.

**Keywords:** Injection Barrier; MWCNT; Rose Bengal Dye; Safranin – T Dye; Threshold Voltage;

Trap Energy

**1. Introduction**

In the past few decades, the study on the physics and chemistry of nanostructures is getting significant attention after the discovery of fullerenes, carbon nanotubes and graphenes. The atypical properties of carbon nanostructures are due to the size effects, which can be seen in zero-dimensional carbon quantum dots, one-dimensional carbon nanotubes, and two-dimensional grapheme layers [1-2]. These nanoscale materials have certain properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts [3]. For carbon nanotubes, the classification can be done on the basis of chirality and also on the basis of number of graphene sheets. In terms of graphene sheets, the carbon nanotubes can be distinguished as single walled carbon nanotubes (SWCNT), double walled carbon nanotubes (DWCNT) and multi walled carbon nanotubes (MWCNT) [4].

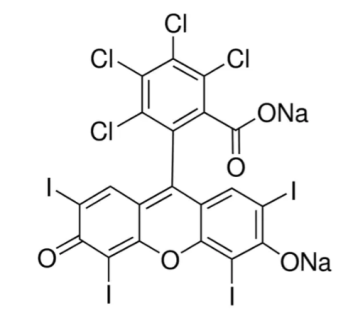
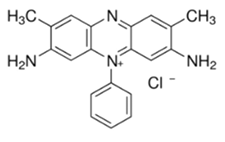
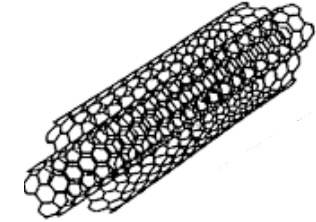
In this present work, we have chosen MWCNT from the family of carbon based nanomaterials (CBN). MWCNT has good electrical conductivity, a large aspect ratio, low mass density and excellent thermal properties [5]. Organic dye based devices have certain excellent attributes such as cost effectiveness, light weight, flexibility and large area device fabrication [6-7]. Despite these attributes, when these organic dyes are sandwiched between two metallic electrodes, the charge flow at the metal – organic contact gets hindered. Poor charge injection can be caused by several factors. Organic devices are predisposed to traps [8]. High trap energy is a significant factor which hampers the flow of charges at the junction area. Injection barrier contributes to lowering of active carrier flow in device. To improve the device performance in terms of lowering of the threshold voltage and enhanced conductivity, reduction of both of these parameters is very much necessary. In this perspective, we have incorporated MWCNT in the organic device, to observe and study its effect on both trap energy and injection barrier. We have selected two organic dyes namely Rose Bengal (RB) dye and Safranin – T dye. As electrodes, we have chosen Indium Tin Oxide (ITO) coated glass substrate and Aluminium (Al). A total of four devices have been prepared with and without MWCNT. Current flow in the prepared devices has been characterized by steady- state current voltage (I –V) plot and it has been analyzed by using Richardson – Schottky (R-S) thermionic emission process [9].

**2. Experimental Details**

**2.1 Materials and Sample Preparation**

RB dye is an anionic dye of xanthenes organic compound [10]. Chemical Abstracts Service (CAS) number and molecular weight of this dye are 632-69-9 and 1017.64 g/mol respectively [11-12]. Safranin - T dye is a cationic azine dye [13]. CAS number and molecular weight of this dye are 477-73-6 and 350.84 g/mol respectively [14]. Empirical formula of this dye is C20H19ClN4 [15]. Fig.1 (a) and Fig.1 (b) illustrate structures of both RB dye and Safranin - T dye. Both these dyes have been bought from Sigma- Aldrich.

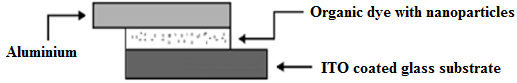
The Multi-walled Carbon Nanotube (MWCNT) is classified as a carbon-based substance that exhibits exceptional physiochemical, thermo-mechanical, and electrochemical characteristics [16]. MWCNT is of 10 µm length and 12 nm of outer diameter. The surface area of MWCNT is 220 m2 /g. The carbon content of MWCNT is more than 98%. CAS number of MWCNT is 308068-56-6 [17]. Fig.1 (c) shows the structure of MWCNT. It has been also bought from Sigma- Aldrich.

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**(a) (b) (c)**

**Fig. 1 Schematic Structures of (a) Rose Bengal (RB) Dye, (b) Safranin –T dye and (c) Multi – Walled Carbon Nanotube (MWCNT)**

Preparation of PVA solution is mentioned in one of our previously published works [18]. PVA acts as an inert binder. RB dye solution is formed by adding 2 mg of RB dye with the prepared PVA solution. After that this RB dye solution is kept in two beakers. In one beaker, there is only RB dye solution and in another, 2 mg of MWCNT is prepended to form the solution with MWCNT and this solution is stirred for one hour. Spin coating process is also mentioned in one of our published works [19]. Organic Device comprising of Safranin –T dye with and without MWCNT has been done by using the similar processes. Fig. 2 shows the structure of organic device. Measurement techniques are similar to one of our published works [20].

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**Fig. 2** **Structure of Organic Device**

**3. Results and Discussions**

Current (I) due to Richardson-Schottky (R-S) thermionic emission can be expressed as

(exp ( -1) (1)

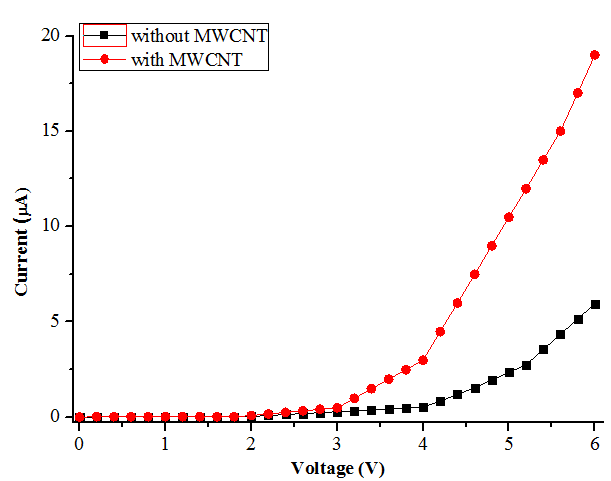
exp () (2)

The above used symbols carry their usual meaning [21-23].

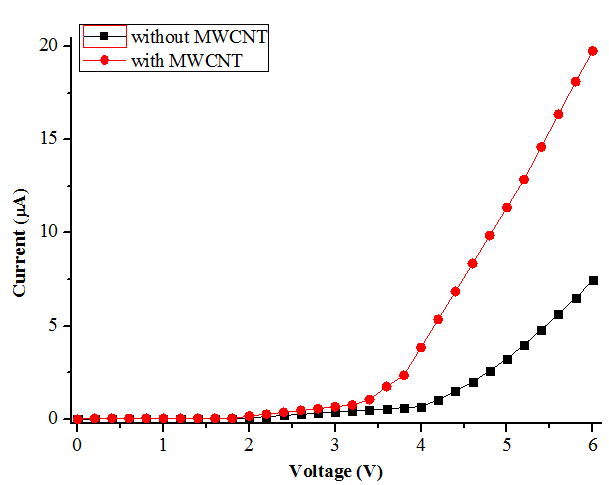
(3)

Fig. 3 (a) and Fig. 3 (b) show the dark I – V characteristics of both RB dye and Safranin – T dye based organic devices with and without MWCNT. With MWCNT, the current flow of RB dye and Safranin – T dye based devices has been increased about 4 times and 3.5 times respectively. Aspect ratio of MWCNT will have paramount effect on both electrical and mechanical properties when it is incorporated in these organic devices. MWCNT acts as conductive fillers of traps resulting in better flow of charge carriers in both of these organic devices.

For estimating injection barrier of these organic devices, semi logarithmic I – V characteristics have been plotted in Fig. 4. Fig. 4 (a) and Fig. 4 (b) show the semi logarithmic I – V plots of both RB dye and Safranin- T dye with and without MWCNT respectively. The value of saturation current ( can be estimated from the semi logarithmic I – V plots and by putting the value of , in equation (3), the injection barriers of both RB and Safranin – T dye based devices in absence and in presence of MWCNT can be estimated.

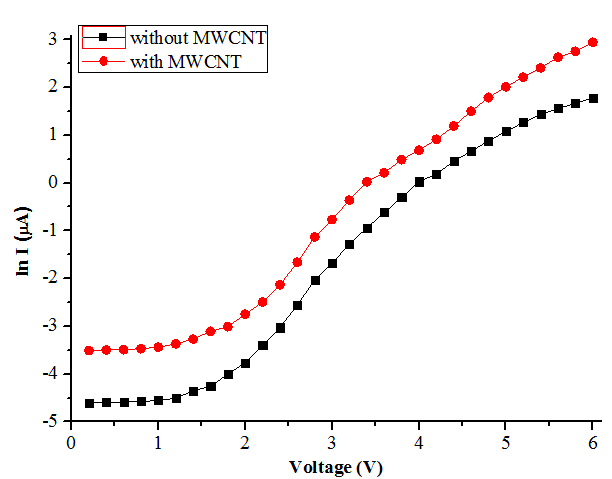
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**(a)**

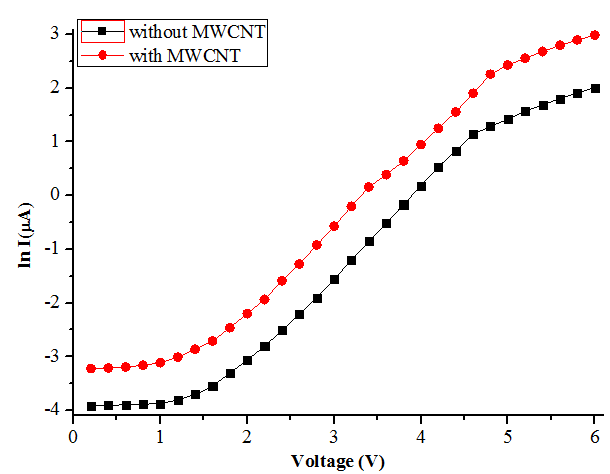
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**(b)**

**Fig. 3 Dark I-V Plots of Devices Comprising of (a) RB dye and (b) Safranin –T dye with and without MWCNT**

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**(a)**

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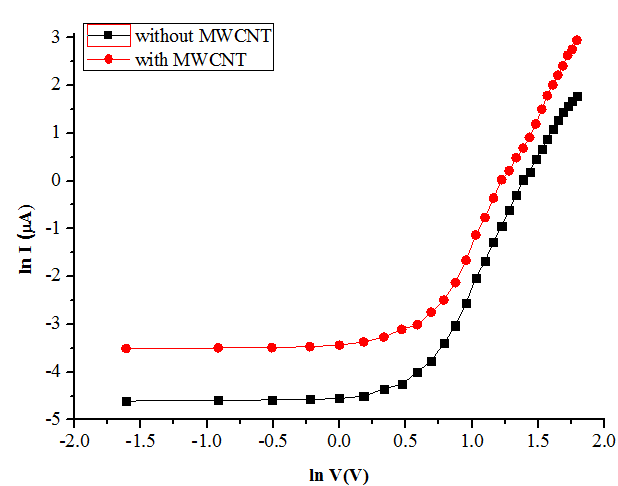
**(b)**

**Fig. 4 ln I – V Plots of Devices Comprising of (a) RB dye and (b) Safranin –T dye with and without MWCNT**

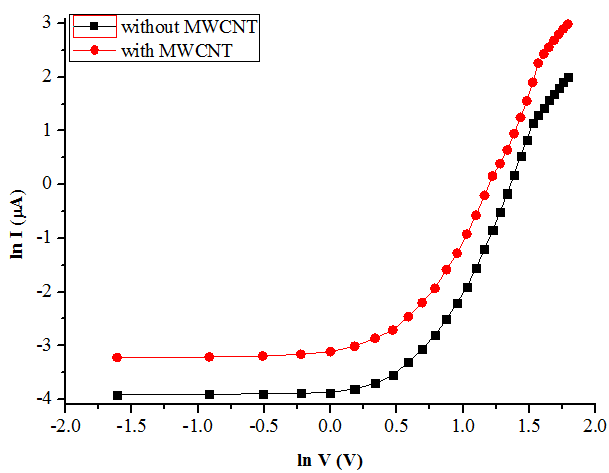
The trap concentration can be estimated by using equation (4)

= (4)

Symbols used here have their usual meaning [24] and m is calculated from both the double logarithmic plot of I -V characteristics of the RB dye based devices and Safranin – T dye based devices with and without MWCNT, which have been shown in Fig. 5.

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**(a)**

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**(b)**

**Fig. 5 ln I- ln V Plots of Devices Comprising of (a) RB dye and (b) Safranin –T dye with and without MWCNT**

The estimation of threshold voltage, trap energy and injection barrier of both the devices in absence and in presence of MWCNT are shown in Table 1.

**Table 1: Estimation of Threshold Voltage, Trap Energy, Injection Barrier for RB dye and Safranin –T Dye Based Devices without and with MWCNT**

|  |  |  |  |
| --- | --- | --- | --- |
| **Organic Device** | **Threshold Voltage (V)** | **Trap Energy (eV)** | **Injection Barrier from Steady State**  **I –V characteristics**  **(eV)** |
| RB Dye | 4.00 | 0.087 | 0.920 |
| RB Dye + MWCNT | 3.00 | 0.075 | 0.860 |
| Safranin –T Dye | 4.00 | 0.059 | 0.810 |
| Safranin –T Dye + MWCNT | 3.50 | 0.047 | 0.790 |

Table 1 shows that, for RB dye, threshold voltage, trap energy and injection barrier estimated from

steady – state I – V characteristics have been reduced to 25%, 13.79% and 6.52 % respectively in presence of MWCNT. For Safranin – T dye also, threshold voltage, trap energy and injection barrier estimated from steady – state I – V characteristics have been reduced to 12.5%, 20.33% and 2.47% respectively with MWCNT. High aspect ratio of MWCNT allows lowering of percolation threshold of electrical conductivity resulting in improving of the device performance by reducing both trap energy and injection barrier at metal – organic contact.

**4. Conclusions**

In this present work, influence of MWCNT on parameters influencing charge conduction process mainly trap energy and injection barrier has been studied. Both the parameters have been decreased significantly with MWCNT. Lowering of both of these parameters will improve the charge flow at the junction area resulting in better conductivity and the devices will be turned on at lower voltages. For both RB dye and Safranin – T dye, incorporation of MWCNT provides more conductive pathways by reducing the trap concentration and injection barrier at metal – organic contact. This present work will be informative to observe and study one of the applications of MWCNT regarding the improvement of charge conduction process of organic device.

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