Evidence of Photoluminescence Quenching in Poly (3-hexylthiophene-2,5-diyl) due to injected charge carriers.

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Abstract

Photoluminescence spectra of Poly (3-hexylthiophene-2, 5-diyl) (P3HT) has been studied in forward and reverse bias direction in a Indium Tin Oxide(ITO)/P3HT/Al schottky device. It has been observed that Photoluminescence quenching is relatively higher in forward direction and the quenching pattern gets reversed when thin insulating layer of Poly (4-vinylphenol) is coated on ITO. The observed behavior of photoluminescence quenching pattern has been explained on the basis of interaction of the injected charge carriers with the excitons generated in the bulk of P3HT together with the interaction of excitons with the applied electric field.

1. Introduction

Research on organic π-conjugated materials is mostly related to its device applications such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and photovoltaic devices [1, 2]. These applications are mainly concerned with charge transport and photo physics. The development of OLEDs basically relies on charge injection and its radiative recombination through exciton formation. Electroluminescence (EL) efficiency is a critical parameter [3, 4] for OLEDs and is directly related to Photoluminescence (PL) efficiency,[5] as both originate from the same intermediate state, i.e., excited state of excitons. While EL emission refers to the spontaneous emission of light by a material under electrical excitation, PL emission on the other hand refers to the spontaneous emission of light by a material under optical excitation. Both EL and PL spectra can be used to characterize a variety of material parameters and other optoelectronic behaviors. Since it is the exciton that forms the basis of both EL and PL, thus exciton dynamics is very much useful for the understanding of OLEDs and photo voltaic effect. A bias dependent PL spectrum thus helps in understanding the mechanism of exciton generation, diffusion and its dissociation simultaneously [6-9]. Moreover, it also provides traces of information regarding electroluminescence, photo-conduction and photovoltaic effects.

Poly (3-hexylthiophene-2,5-diyl) (P3HT) is one of the preferred conjugated polymer for the purpose of Organic Field Effect Transistors (OFETs), [10] organic photo induced memory devices [11, 12] and photovoltaic devices [13-15]. It is known that Aluminum

(Al) forms a schottky type contact with P3HT. This type of contact has particularly been well exploited for photovoltaic and other related effects. Thus a detailed study of a schottky junction assumes critical importance for a clear understanding of the dynamics of exciton. In this paper P3HT based schottky cell i.e. ITO/P3HT/Al, as shown in Fig.1(a) and referred to as (cell A) was studied. The various possible competing mechanisms for the exciton dissociation have been discussed. The proposed mechanism was further verified using another type of cell ITO/PVP/P3HT/Al (cell B) as is shown in Fig. 1(b).

2. Experimental

For the purpose of Schottky cell fabrication, etch patterned ITO coated glass was taken as the substrate, which was subsequently sonicated in chloroform and iso propanol solution. It was then spin coated with a chloroform solution of P3HT, which was used as obtained from Merck (Lisicon SP001). A uniform and 200 nm thick P3HT film was coated on top of these patterned ITO electrodes. Later the device was coated with 6 mm wide and 30 nm thick Aluminum (Al), by thermal evaporation technique, patterned perpendicular to the bottom ITO electrode. For the cell B all the other steps were identical except that in this case ITO was coated with a Poly (4-vinyl phenol) (PVP) film, followed by its cross linking [16], prior to spin coating the P3HT. Thickness of PVP and P3HT were later estimated to be 500 nm and 200 nm respectively, as measured using Dektak surface profiler. Keithley 6517A electrometer was used for the IV measurement. PL measurement was done under ambient condition using Hamamatsu photonic multi

channel analyzer; model C7473, kept at a distance of 70 cm from the sample. A 300 mW, class III B, CW, He-Cd laser, 442 nm, model IK4121R-G by Kimmon Electric Company Limited, was used as a light pumping source. The intensity of the laser radiation falling on the sample was attenuated to be 0.15 W/cm^2.

3. Results and Discussion

In our previous work [12] a PL quenching due to Aluminum coating on the top of P3HT film was observed. This effect was attributed to the fact that Al forms a depletion layer with P3HT [17, 18], leading to the decrease in the intensity of PL signal. It is this depletion layer that gives ITO/P3HT/Al cell a rectifying behavior resulting in a diode like current voltage characteristics. It can therefore be argued that applying electric field to a Schottky cell results in changing depletion width. Depletion layer can also be regarded as a dead layer for PL emission [19]. Hence, changing the depletion layer width results in changing the width of active bulk region of the P3HT. Since PL is basically a study of spontaneous emission from the active region of the bulk film, hence changing bulk layer thickness would result in the observable changes in the PL signal. The radiative PL efficiency η_{PL} is defined as,[20, 27]

$$\eta_{PL} = \left(\frac{K_R}{K_R + K_{NR}} \right) \text{—} \tag{1}$$

The bias dependent PL quenching Q_{PL} [23, 24] is defined as

$$Q_{PL} = \left(I_{PL}(0) - I_{PL}(V) \right) / I_{PL}(0) \tag{2}$$

Where $I_{PL}(0)$ and $I_{PL}(V)$ denotes the PL emission intensity at zero bias and at applied bias voltage V, respectively. Further, PL intensity I_{PL} relates to η_{PL} [27] by the eq (3)

$$I_{PL} = I_{abs}\eta_{PL}\eta_{C} \tag{3}$$

Where I_{abs}, η_{PL} and η_{C} denotes the intensity of the absorbed laser light, the radiative PL efficiency and the photon capturing efficiency of the detector respectively. Under these conditions the PL intensity I_{PL} is directly proportional to the absorbed light intensity I_{abs}. It was found that double excitation of the films occurred when they were coated with Al top layers having a reflection coefficient R. Thus, the intensity of the absorbed light by the P3HT bulk is the difference of the incident light intensity and the sum total of the transmitted and the reflected light intensity from the cell. The absorbed light intensity I_{abs} is given by eq (4) [27],

$$I_{abs} = I_0\chi\left(1 - (1-R)e^{-\alpha x} - \mathrm{Re}^{-2\alpha x}\right) \tag{4}$$

Where I_0 is the incident laser intensity, R denotes the reflection coefficient of Al top layer and its value has been found to be 0.92 for a 30 nm thick Al over layer, χ is the scaling factor, which arises probably due to the interaction of laser light with the depletion layer, although the exact nature of such an interaction is not yet completely understood. It has been observed that $\chi = 1.5$ yields a good agreement with the observed results. α denotes the absorption coefficient of the P3HT film (at $\lambda = 442$ nm), while x denotes the penetration distance of the laser beam as measured from ITO electrode in the direction of the thickness of the film.

The PL Quenching for cell A along with its *I-V* characteristic has been shown in Fig. 2. Higher level of PL quenching was observed in the forward direction as compared that observed in the reverse bias direction. Similar results were obtained by Majumdar et al [26]. We attribute higher level of quenching in the forward direction to the probable interaction between the excitons and injected charge carriers in the bulk of P3HT. The reverse bias quenching has been explained on the basis of the increasing thickness of the depletion layer upon the application of reverse bias. Figure 3 shows the plot of quenching as well as *I-V* for the cell B which includes ITO covered by PVP. A perusal of Fig. 3 clearly indicates that inclusion of PVP leads to decrease in the current level in cell B and most importantly the quenching pattern of the cell B is reversed. A higher level of quenching is found to occur in cell B under the reverse bias conditions as compared to the quenching level under the forward bias condition.

In order to clearly understand the mechanism behind the PL quenching under the forward direction ln *J* vs. ln *V* has been plotted for both the cells A and B as shown in Fig. 4. It has been found that the quenching is more pronounced in cell A under the forward bias condition, which may be due to the higher number of injected charge carrier in this cell. It can be clearly seen from the Fig. 4 that the injected charge carriers in cell A is almost three orders of magnitude higher than that in cell B. It is a clear evidence of the role of the injected charge carrier in the PL quenching. Although further investigation is needed in this regard to completely establish the relationship between the number of injected charge carriers and quenching in the respective cell. It must also be noted that in the case of cell B the contribution in current mostly comes from impurity and the thermally generated charge carrier as its slope is linear. In case of cell A the slope suddenly changes

and the device transforms from ohmic to non-ohmic region, a clear signature of injection taking place in cell A and not in cell B. From these above mentioned discussions it can be concluded that the injected charge carriers interact with the excitons and hence result in PL quenching.

Upon combining eq (2, 3 and 4) and solving we get,

$$\delta w(V) = \frac{1}{\alpha} \ln \left| \frac{\sqrt{(A+2B)^2 + 4BQ_{PL}} - A}{2B} \right| \tag{5}$$

Where the values of A and B were 0.07, 0.46 respectively and α was determined experimentally using UV-visible spectra to be 32000 cm^{-1} and $\delta w(V)$ denotes the change in the depletion width due to change in the bias across the depletion width. The values of $\delta w(V)$ plotted against voltage V has been shown in Fig. 5. It exhibits that modulation of depletion width by the application of reverse bias is less pronounced in cell B as compared to that of cell A. It could probably be because of a lesser field drop across the schottky junction in cell B due to the inclusion of an insulating layer of PVP over the ITO electrode. Therefore it can be concluded that depletion layer width is directly related to the PL quenching under the reverse bias condition. However as is well known under the application of the forward bias the depletion width decreases slightly below the built in Voltage V_{bi} and above which it remains constant [25], which means an increase in the bulk active region of P3HT results in higher values of I_{abs} and thus leading to increased PL intensity in the region between $0 < V < V_{bi}$. However, it must be noted that such a behavior is characteristic of inorganic semiconductors [21, 22]. In some earlier reports a PL quenching [5], Q_{PL} (decrease in the intensity of PL emission) for organic

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semiconductor materials was observed as electric field was applied on to the schottky cell, irrespective of the direction of applied bias.

4. Conclusion

Two types of cell ITO/P3HT/Al (A) and ITO/PVP/P3HT/Al (B) have been fabricated for the purpose of bias dependent PL study. The quenching pattern obtained in the two cells was just opposite of each other. In cell A relatively higher quenching was observed under forward bias condition, however in cell B the relatively higher quenching occurred under reverse bias condition. It was concluded that presence of charge carriers cause quenching in the forward direction, as was demonstrated by cell B. Thus in general the quenching in the forward direction of cell A has contributions from Electric field as well as bulk charge carriers; although under reverse bias the quenching is mainly due to the increasing depletion width. The results are of critical importance for the better understanding of the optoelectronic behavior of P3HT, and the possible related applications. The results presented here also demonstrate the possible current induced defects related PL quenching a characteristic of polymeric materials.

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Figure Captions

Fig. 1 Schematic diagram of (a) cell A and (b) cell B.

Fig. 2 A plot of Quenching (*Q*) versus Voltage (*V*) and *IV* characteristics of cell A.

Fig. 3 A plot of Quenching (*Q*) versus Voltage (*V*) and *IV* characteristics of cell B.

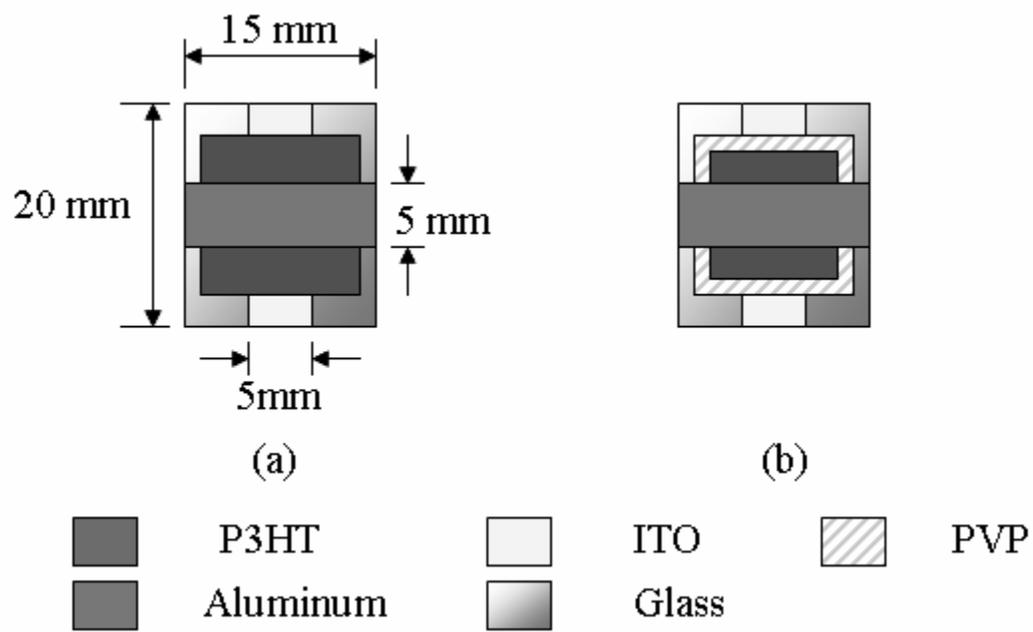Fig. 4 A plot of ln J vs. ln V for cell A and B.
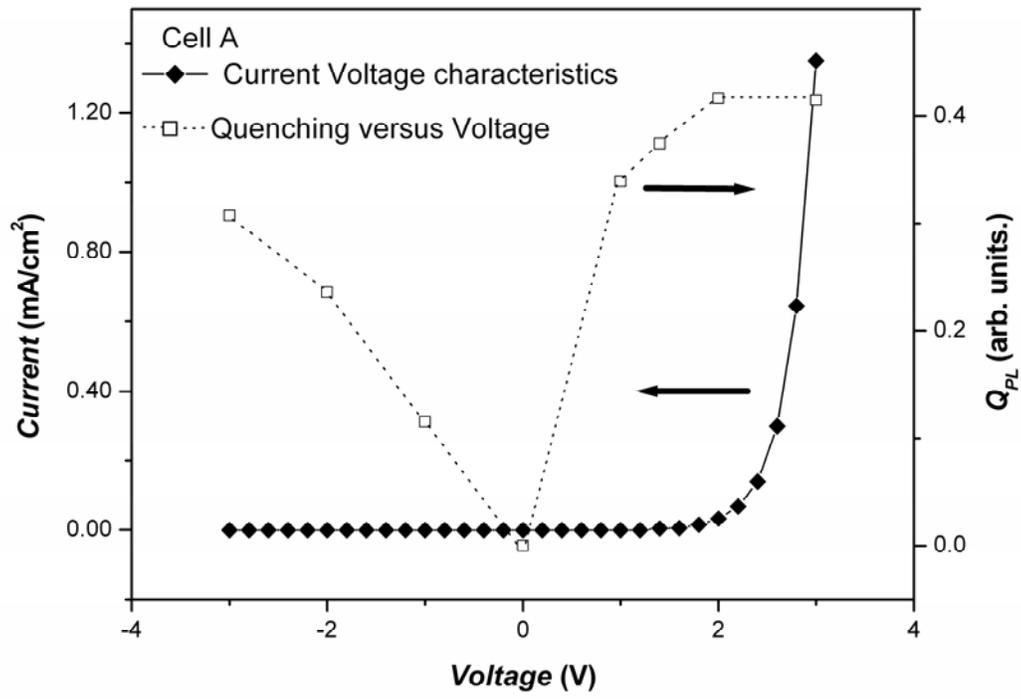
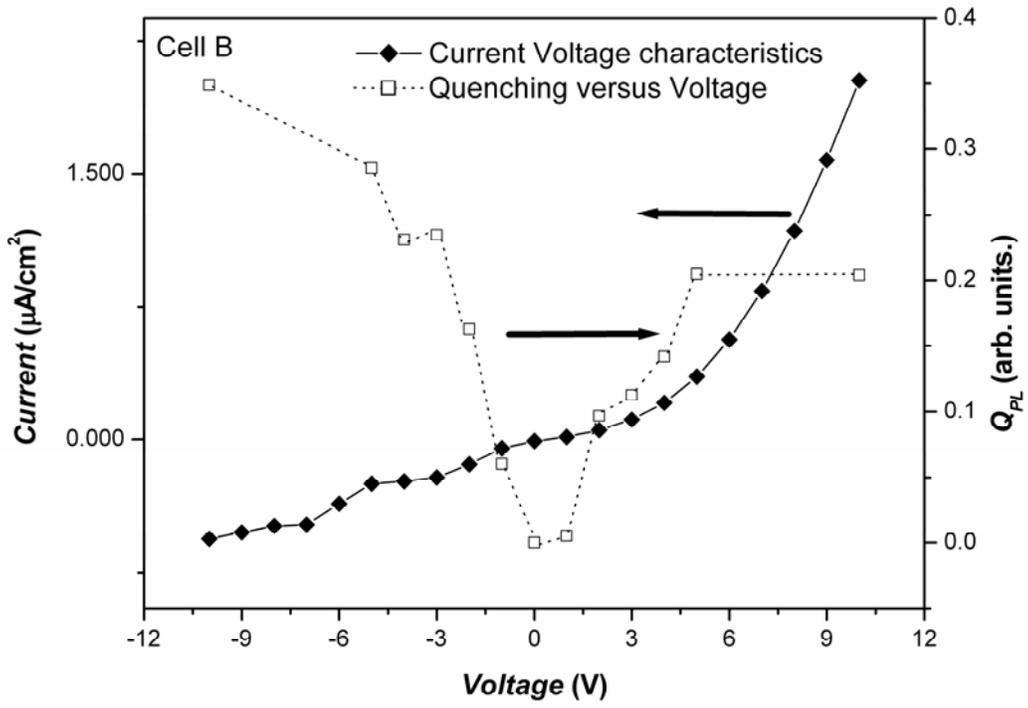Fig. 5 Plot of $\delta w(V)$ versus Voltage (*V*) for cell A and B.
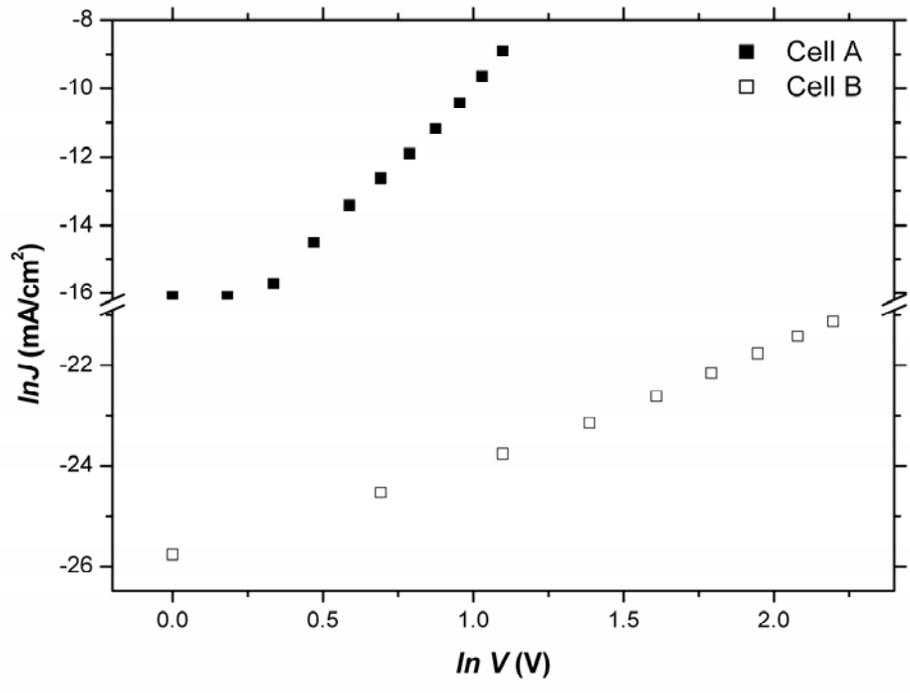
Fig.1

Fig. 2

Fig. 3

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Fig. 5