Charge generation and photovoltaic properties of thin film device based on pyronine G:zinc oxide composite

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The electrical and photoelectrical properties of thin film hybrid blend device consisting of nanocrystalline inorganic semiconductor zinc oxide (ZnO) and pyronine G (PYR G) (an organic p-type semiconductor) have been studied through recorded fluorescence (FL) spectra, current-voltage characteristics (in dark and under illumination) and photo-action spectra of device. The quenching of FL spectra of PYR G when mixed with ZnO has been interpreted in terms of efficient electron transfer between PYR G (donor) and ZnO (acceptor) on photoexcitation. The observed results justify the formation of bulk heterojunction between PYR G and ZnO, sandwiched between Al and ITO electrodes. The nearly linear dependence of photocurrent with incident light intensity suggests the efficient photo-induced charge-transfer in the device consisting of PYR G:ZnO restricting charge recombination comparatively to device based on pure PYR G. The absorption spectra of the blend suggest the formation of hetero-junction and there is no ground state doping.

Keywords: Photo-induced charge transfer, Bulk heterojunction, Photovoltaic effect, Fluorescence, Quenching

1 Introduction

Organic materials in the form of thin films have promising photovoltaic applications\textsuperscript{1-4}. In recent years, both conjugated polymers and small molecules based photovoltaic devices have been investigated\textsuperscript{5-10}. Firstly organic solar cells were prepared from small molecules based on merocyanines and phthalocyanines as single layer thin film devices, mainly in Schottky barrier arrangement\textsuperscript{1}. The power conversion efficiency of these devices hardly reached 1%. One of the most important advantages of organic semiconductors over their inorganic counter parts is their ability to be processed in solution, which enables the use of effective deposition techniques, such as spin coating\textsuperscript{11-12}. The photogeneration yield (generation of electrons and holes due to light absorption) in pure organic semiconductors is insufficient. One approach to achieve an efficient charge carrier generation in organic light absorbers is to blend them with suitable acceptors. Recently several groups have achieved power conversion efficiencies for organic solar cells approaching 4% over the absorption region of polymer using either polymer-polymer\textsuperscript{4,6,12-14} or polymer-nanoparticles\textsuperscript{15-17} blends to improve exciton dissociation. Work on photovoltaic device based on blend composite is encouraging, though the quantum efficiencies are still significantly below either Si or dye sensitized electrochemical cells\textsuperscript{18} wherein the use of an electrolyte impose another serious technological complications.

In this paper, nanocrystalline ZnO (nc-ZnO) as n-type semiconductor and pyronine G (PYR G) as p-type organic material are used as both active photogeneration medium and hole transporter, in hybrid bulk heterojunction solar cell. ZnO has high electron mobility even when measured on films consisting assembled ZnO nanoparticles. The electrical and photovoltaic properties of PYR G:ZnO thin films sandwiched between ITO and Al electrodes have been studied. The photogeneration process in the devices is investigated by the comparison of photoaction spectra of device illuminating through the ITO and Al side with absorption spectra of the blend and further comparison of fluorescence spectra of PYR G and PYR G:ZnO. A strong fluorescence quenching is observed in the PYR G spectra when PYR G is mixed with ZnO, which suggests the formation of long lived positive polaron on PYR G as a consequence of electron transfer from PYR G to ZnO upon photoexcitation.
2 Experimental Details

The blend of zinc oxide (ZnO) and pyronine G (PYR G) were prepared by dissolving ZnO and PYR G (1:10) by weight in methanol solution. The thin film of this blend was fabricated by spin coating over ITO coated glass substrate. Upon annealing this film to 100°C, the ZnO particles sintered together. The thickness of the films is about 400 nm. The absorption and fluorescence spectra of the PYR G and PYR G: ZnO were recorded on Hitachi fluorescence spectrophotometer (Model F 3000). The counter electrode (Al) was deposited on the top of blend film by thermal evaporation under vacuum of 10⁻⁶ torr. The electrical transport in ITO/ZnO: PYR G/Al device is studied via current density –voltage (J-V) characteristics using Keithley Electrometer (610 C) with built in voltage source by applying negative and positive voltage across ITO and Al, respectively. The device transport in ITO/ZnO: PYR G/Al device is studied via current density –voltage (J-V) characteristics using Keithley Electrometer (610 C) with built in voltage source by applying negative and positive voltage across ITO and Al, respectively. The J-V characteristics data were taken in dark and under white light illumination provided by a halogen lamp source through ITO electrode and light intensity was varied from 1 to 300 mW/cm². A photo-action spectrum of the device was taken using a halogen lamp source and monochromator and resulting current was measured employing Keithly Electrometer (610 C). The light intensity of the incident light was measured employing Luxmeter. The cyclic-voltammetry (CV) of PYR G was carried out in three electrode cells consisting of a platinum (Pt) working electrode, a Pt counter electrode and Ag/AgCl reference electrode using sweep rate 10-15 mV/s.

3 Results and Discussion

Efficient charge transfer from donor to acceptor component, effective charge transport and charge injection into electrodes are important parameters for the design and optimization of organic photovoltaic devices. In this regards, electrochemical data can give valuable information and can be estimated by the relative position of HOMO/LUMO levels of organic semi conducting materials. The information about these levels plays an important role for the selection of suitable donor-acceptor pairs. We have estimated the values of these levels from cyclic-voltammetry (CV) experiment. The onset values for oxidation and reduction potential of PYR G are estimated as +1.28 and −1.12 V, respectively. The corresponding values of HOMO and LUMO levels for the PYR G were calculated using $E_{1/2}$ for measurements in solution. The values of HOMO and LUMO levels are found to be −5.2 and 3.8 eV, respectively and the corresponding band gap calculated from cyclic-voltammetry measurements is about 2.4 eV. The band gap calculated from the CV measurement is lower than that calculated from optical absorption spectra.

The photo-induced charge separation has been studied by fluorescence spectroscopy and absorption spectra of the material. The absorption spectra of PYR G have the absorption edge at 340 nm and absorption peak at 540 nm. The absorption edge at 340 nm corresponds to π-π* transition while the absorption peak at 540 nm corresponds to the π-π* transition. The molecular system of PYR G shows the phenomena of extended conjugation which is in fact responsible for its absorption in the longer wavelength i.e. at 540 nm in the visible spectrum. Two electronic structures are possible in which the conjugation is totally different, one where the oxygen assumes positive charge and other possible structure where the nitrogen assumes positive charge. However, because nitrogen is less electronegative than oxygen the former can support a positive charge more easily than the latter and therefore, the structure with positive nitrogen is more likely one. Therefore, we assume that the predominant electronic transition in the molecular system of PYR G is π-π*. The band gap of PYR G was calculated from the variation of ($ahv$)² with $hv$ about 2.45 eV as reported by Sharma et al.¹⁹

ZnO is an inorganic semiconductor and strongly absorb UV light (380 nm) but transmit visible light. The mechanism of UV absorption in the material involves the use of photon energy to excite electrons from valence band to conduction band. ZnO has band gap of about 3.3 eV which corresponds to wavelength of 380 nm. The UV-visible spectra of PYR G:ZnO blend clearly reveal the presence of PYR G from the strong π- π* transition in the visible region. We have found that with the increase of ZnO amount in the blend, the absorption maximum of the blend shifts towards the shorter wavelengths. This is possibly due to the ZnO prevents aggregation of PYR G conjugation in solid state.

The fluorescence spectra of the PYR G and PYR G:ZnO thin films coated on glass plate were excited at 540 nm. A pure PRY thin film exhibits a maximum fluorescence at 630 nm. However, no fluorescence was observed in PYR G thin film containing 10% (by weight) of ZnO. The fluorescence is strongly quenched by addition of ZnO, which is due to the fast de-activation of the excited state by electron transfer reaction. This implies a high charge generation efficiency in the blend of PYR G: ZnO enabling the separation of charges before radiative recombination.
The current-voltage ($J-V$) characteristics in dark and under illumination of PYR G:ZnO composite device are shown in Fig. 1. In this device the PYR G:ZnO composite was sandwiched between ITO and Al and a negative and positive bias is applied to ITO and Al electrodes, respectively. The $J-V$ characteristics in dark show excellent diode behaviour, with a rectification ratio of about 200 at 1.5 V. The forward current density through PYR G:ZnO layer is considerably higher than that for pure PYR G which indicates that the current due to electrons dominates the forward bias current. This supports the appearance of a continuous path way for electron transport through the nc-ZnO network. Similar results have been reported for MDMO:ZnO composite device. The $J-V$ characteristics can be separated into three regions: (i) Under reverse bias and forward bias up to turn on voltage, the characteristics are dominated by the leakage current and behaves almost symmetrically, (ii) At a voltage corresponding to the condition, when the interface barriers can overcome, the current starts to increase exponentially with applied forward voltage and (iii) At voltages exceeding the flat band conditions, the current saturates and is space charge limited and follows the $J \propto V^m$ with $m \geq 2$, law.

A remarkable enhancement in the photovoltaic response has been observed in the device consisting of PYR G :ZnO with respect to the device with pure PYR G as reported by Sharma. This is due to the formation of bulk heterojunction which is spread all over the volume sandwiched between Al and ITO. The photovoltaic parameters-short circuit photocurrent density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$) and power conversion efficiency of the Al/PYR G:ZnO/ITO are presented in the Table 1. For the comparison the photovoltaic parameters for Al/PYR G/ITO device were also presented in Table 1. We have observed higher photocurrent densities and external quantum efficiencies for device consisting of hybrid material. This can be interpreted in terms of formation of hetero-junction throughout the bulk, leading to more efficient exciton dissociation which is reflected in the slightly higher open circuit voltage ($V_{oc}$). The improvements in short circuit current density and quantum efficiency are due to the rough surface and increased surface area in hybrid material. The increased surface area of the dissociation interface leads to higher charge extraction from the device and a subsequent decrease in charge recombination.

The photogeneration of charge carriers in the device were studied by spectral response of photocurrent (variation of photocurrent with wavelength) measurements. For the comparison we have shown the spectral response of device consisting of pure PYR G in Fig. 2. From the comparison of photoaction spectra of Al/PYR G/ITO device with the optical absorption spectra of the PYR G thin films, it is observed that the PYR G behaves as $p$ type organic

![Fig. 1 — Current-voltage characteristics of the ITO/PYR G:ZnO/Al device in dark and under illumination](image1)

![Fig. 2 — Photoaction spectra of Al/PYR G/ITO device illuminating through Al and ITO side](image2)

### Table 1 — Photovoltaic parameters for devices

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Al/PYR G:ZnO/ITO Device</th>
<th>Al/PYR G/ITO Device</th>
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<tr>
<td>Short circuit photocurrent ($J_{sc}$)</td>
<td>0.15 mA/cm$^2$</td>
<td>1.22x10$^{-7}$ A/cm$^2$</td>
</tr>
<tr>
<td>Open circuit voltage ($V_{oc}$) (V)</td>
<td>0.84</td>
<td>0.75</td>
</tr>
<tr>
<td>Fill factor ($FF$)</td>
<td>0.53</td>
<td>0.41</td>
</tr>
<tr>
<td>Power conversion efficiency (%)</td>
<td>0.63</td>
<td>0.044</td>
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semiconductors which form the ohmic contact and Schottky barrier with ITO and Al, respectively. The maximum response of device based on pure PYR G does not correlate with the maximum absorption of PYR G under illumination through ITO side (antibatic), while the response of device consisting of PYR G:ZnO blend matches with the absorption (symbatic) when illumination is through both Al and ITO side. The photocurrent in the region below 380 nm is due to the absorption of photons by ZnO and subsequent injection of electron from valence band to conduction band of ZnO. However, above this wavelength, the photocurrent is due to the absorption of photon by PYR G:ZnO composite and that is responsible for producing excitons. These excitons subsequently get dissociated into free electrons and holes and these electrons and holes are transported through ZnO and PYR G, respectively, towards their respective electrodes. These results also suggest the formation of bulk heterojunction between ZnO (acceptor) and PYR G (donor) and PYR G:ZnO which is spread over whole volume sandwiched between ITO and Al. On photoexcitation efficient electron transfer between PYR G and ZnO takes place. The photoinduced charge transfer in the device leads to an increase in fill factor and power conversion efficiency. In this blend, the distance that an exciton cover to reach an interface is typically very short and thus efficient charge separation is achieved for all absorbed photons. Light is absorbed mainly by PYR G as ZnO has little absorption in the visible region of spectrum (above 380 nm). Excitons that are created in PYR G quickly get separated into free electrons and holes and then transported through a combination of drift and diffusion to their respective electrodes. The region of light sensitivity also broadens with the incorporation of ZnO.

The increase in short circuit photocurrent for composite blend device is due to efficient photoinduced charge transfer between donor (PYR G) and acceptor (ZnO). The increased quantum efficiency in this device is due the increased surface area of the dissociation interface which leads to higher charge extraction from the device and a subsequent decrease in charge recombination. In a device consisting of ITO /PYR G /Al, the internal field created by the difference in the electrode work functions is such that holes exit through the ITO and electrons are drawn to opposite electrode (Al), when operated in open circuit mode. For light incident through ITO, holes will immediately exit through ITO, while electrons must travel through the entire organic layer to reach opposite electrode i.e. Al. Low electron mobility in organic materials leads to lower efficiency and fill factor however, in the device ITO/PYR G:ZnO/Al, there is a formation of bulk heterojunction between ITO and Al wherein excitons created by light absorption within the PYR G would have a small distance to diffuse before reaching the donor-acceptor interface. Once dissociation occurs, electrons are immediately transferred to ZnO and holes to PYR G, reducing the chances of recombination. This leads to efficient photoinduced charge transfer in the blend resulting higher quantum efficiency and fill factor.

We have studied the light intensity dependence of short circuit photocurrent ($J_{sc}$) for Al/PYR G/ITO and Al/PYR G:ZnO/ITO devices. The dependence of $J_{sc}$ on light intensity ($P$) in both devices follow the power law i.e. $J_{sc} \propto P^m$ with power factor (m) is 0.61 and 0.94 for Al/PYR G/ITO and Al/PYR G:ZnO/ITO devices, respectively. The increases in power factor for composite device also confirm the formation of bulk heterojunction and efficient photoinduced charge transfer in the device. This nearly linear relationship for the device consisted of PYR G:ZnO implies that only minor charge carrier recombination is occurring in comparison to the device based on pure PYR G.

The exciton diffusion length in PYR G is also estimated by means of fluorescence intensity at different PYR G thicknesses on coated ZnO electrode and PYR G on ITO coated electrode. The PYR G thickness on ZnO layer is estimated from the UV-visible optical absorption of the layer using known absorption coefficient of PYR G. The fluorescence varies linearly with PYR G thickness on ITO and approximately linear with PYR G thickness on ZnO. The complete quenching of fluorescence at a layer of thickness about 22 nm was observed and therefore we have estimate exciton diffusion length in PYR G which is about 22 nm. This is similar to that of MEH-PPV and longer than fluorine-thiophene.

The photoinduced charge transport in the composite can be explained employing the energy band diagram as shown in Fig. 3. There are two processes taking place under illumination: (a) Photons below wavelength 380 nm are absorbed by ZnO and the electrons are injected into conduction band from the valence band of ZnO, and subsequently collected by Al electrode (low work function). The holes in the valence band of ZnO are diffuse towards the PYR G due to potential gradient and finally collected by ITO.
electrode (high work function). (b) The photons above the 400 nm are absorbed by PYR G in PYR G: ZnO composite and create excitons which get dissociated into free carriers due to bulk heterojunction. Then the electrons are transferred into conduction band of ZnO and holes transported through PYR G. The electrons in conduction band of PYR G transferred to ZnO and immediately collected by Al electrode while the holes in valence band of PYR G collected by ITO. Electrons and holes follow different path, therefore the recombination is avoided leading to the improved photovoltaic response.

The relative positions of donor LUMO and acceptor LUMO is crucial for effective charge transfer. As shown in Fig. 3, there is a difference of 0.6 eV between LUMO of PYR G and conduction band of ZnO (4.4 eV). HOMO of PYR G is clearly higher in energy than for valence band of ZnO. These conditions indicate that excitons dissociation of photoexcited PYR G via electron transfer may occur at the interface with ZnO, enabling the photogeneration of electrons and holes. Therefore, PYR G can be used as an electron donor with ZnO as an electron acceptor to fabricate donor: acceptor interpenetrating bulk heterojunction photovoltaic device.

4 Conclusions
We have reported the charge generation and photovoltaic properties of PYR G: ZnO hybrid thin film sandwiched between Al and ITO. A significant photocurrent is achieved which is due to the efficient photoinduced transfer of electrons from PYR G to ZnO in the bulk of thin film. The enhancement in photovoltaic response of the Al/PYR G:ZnO/ITO device has been explained in terms of the formation of bulk heterojunction between PYR G (donor) and ZnO (acceptor) interpenetrating network, which is spread over the whole volume sandwiched between Al and ITO electrodes and leading to larger surface area for efficient exciton dissociation. The strong fluorescence quenching in the PYR G:ZnO composite in comparison to pure PYR G, when excited at 540 nm also suggests the formation of donor: acceptor interpenetrating network. In the present device, significant photocurrent generation is achieved due to the collection of electrons from ZnO at Al electrode and holes are collected at ITO electrode. ZnO nanoparticles can be dispersed in polar solvent mixtures and therefore, be easily blended with PYR G and can be utilized for efficient photovoltaic devices.

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