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Bulk heterojunction formation with induced concentration gradient from a bilayer structure of P3HT:CdSe/ZnS quantum dots using inter-diffusion process for developing high efficiency solar cell

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ABSTRACT

Bulk heterojunction (BHJ) solar cells consisting of poly(3-hexylthiophene) (P3HT) as donor and cadmium selenide/zinc sulphide (CdSe/ZnS) core shell quantum dots (QDs) as acceptor have been developed. Starting from the bilayer of P3HT/QD structure a BHJ is induced using the process of thermal inter-diffusion. The absorption measurements on the bilayer structure show that the absorption coefficient increases and the absorption spectrum becomes broader in the annealed device. Also, the photoluminescence of the annealed device is found to decrease by an order of magnitude showing a significant transfer of electrons to the QDs. With this approach and under broadband white light with an irradiance of 8.19 mW/cm^2, we have been able to achieve a power conversion efficiency of 5.1% and fill factor 0.45 for this solar cell.

1. Introduction

Organic photovoltaic (OPV) devices have been investigated by a large number of workers as an alternative to inorganic semiconductor based devices [1–6]. Despite the fact that the operating life of organic solar cells is extremely low (<10^4 h) and their photo conversion efficiency (PCE) is relatively low (the maximum single layer PCE reported is 6.4% [6] and to be able to compete with crystalline solar cells, commercially, a minimum PCE of 10% is required for OPV), there are strong motivations for working in the area of OPV such as their low cost, easy and environment friendly processing techniques, high mechanical strength, extremely high flexibility and lightweight.

The basic practical OPV device is a bulk heterojunction (BHJ) consisting of an interpenetrating network of electron donor and electron acceptor materials in which both the components are phase segregated and are distributed in three dimensions on a nanometric scale with spatial distance between the donor and acceptor molecules <10 nm (less than diffusion length of excitons in the photoactive donor material). This structure, which is formed during spin coating from a common solvent, was first proposed by Saraciftci et al. [7]. The electron donor usually is a conducting polymer such as poly(3-hexylthiophene) (P3HT) or poly(3-octylthiophene) (P3OT), which has high absorption coefficient in the visible region of the solar spectrum with high mobility of photo generated holes and the electron acceptor usually is a fullerene derivative such as C_{60} or [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). The device performance depends on how fast the photo-generated excitons at the surface of donors are dissociated and how fast the dissociated holes and electrons are carried

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to the respective electrodes. The dissociation of excitons requires a highly favorable and appropriate lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of the two components. The photo generated charge separation requires high mobility and good morphology for both the components making the BHJ. It is extremely difficult, however, to fabricate a BHJ structure where an ultra fast transfer of photo-generated carriers can be achieved due to the following reasons:

1. Usually the two components of the BHJ *viz.* donors and acceptors are grown in either amorphous or polycrystalline phase. Their morphology depends on the evaporation rate of the solvent. If it is too fast the morphology is amorphous and if the evaporation rate is too slow, the grown donor and acceptor domains are much larger than the diffusion length of the excitons. Photo generated excitons then get lost without having an opportunity to dissociate into free holes and electrons [8].
2. If the morphology of the film is poor, the holes will have low mobility and therefore concentration of the electrons and holes will not be balanced. In such a situation the device current is space charge limited and the fill factor is lowered resulting in poor performance of the PV device [9].
3. It is extremely necessary to keep right concentration of the two components to achieve the phase segregation. The concentrations have to be calculated on the basis of thermodynamical phase diagram. Muller et al. [10] were the first to calculate theoretically the tertiary phase diagram for obtaining BHJ of P3HT and fullerene. However, it is almost impossible to maintain the concentrations that meet the thermodynamical requirements of the two components of the BHJ because during spin coating of the composite film, their concentration starts changing with the evaporation of the solvent.
4. The domains of the two components start growing in size with age, i.e., time after fabrication, reducing the surface area available for exciton dissociation and charge separation. The BHJ–OPV devices, therefore, deteriorate rapidly with time.

Some workers have used bilayer [11] as well as composites [12] of P3HT and CdSe QDs for fabrication of solar cells, however, the resulting PCE of the cells was observed to be very low (<1%). It was demonstrated by Drees et al. [13] that it is possible to induce a BHJ by thermal diffusion at appropriate temperature from a bilayer structure of P3HT and C_{60}. As evidence of charge transfer from donor to acceptor these authors used photoluminescence (PL) measurements of the donor P3HT, which decreases by about an order of magnitude when the BHJ was formed. Also the photoconductivity of the bilayer system and short circuit current of the solar cell was found to increase by more than an order of magnitude when thermal annealing is optimized leading to the formation of BHJ. These authors also studied the morphology of the inter-diffused bilayer film from anode to cathode using cross-sectional transmission electron microscopy. It was found by them that inter-diffusion from the two layers leads to the formation of BHJ with a concentration gradient of donors and acceptors.

In the present work, we have attempted to create a BHJ for a P3HT–cadmium selenide/zinc sulphide (CdSe/ZnS) core shell quantum dots (QDs) bilayer using the concept of thermal diffusion for fabricating a hybrid organic–inorganic solar cell structure. The process of inter-diffusion is highly sensitive to the temperature at which the samples are annealed. The temperature at which the BHJ is formed must be higher than T_g but lower than T_m where T_g is the glass transition temperature of the conducting polymer and T_m is its melting point. By optimizing the temperature and duration of the diffusion process, a PCE of 5.1% and fill factor of 0.45 was achieved for our solar cell samples.

This hybrid PV device has the following advantages over the OPV devices consisting of P3HT:PCBM BHJ:

1. The QDs can provide an additional source of absorption of solar spectrum in the visible region. This spectral range can be tuned by changing the size of the QDs [14].
2. Multiple excitons can be created when a single photon having energy much higher than the bandgap is absorbed by the QDs by the process of impact ionization [15]. The resultant charge carriers, on dissociation of the excitons, must be collected at the electrodes before they recombine. For impact ionization to happen the energy difference between the discrete quantized energy levels of the QDs should be higher than the energy of the longitudinal optical phonons so that the relaxation dynamics of the high-energy photo-generated charge carriers is slowed down [16]. The PCE of the device can thus be increased.
3. If LUMO and HOMO levels of the organic conducting polymer are favorable with respect to the conduction and valence band of the QDs, the exciton dissociation will be fast. Also, if the morphology of the film is good and smooth (free from overlapping of polymer chains, kinks and several discontinuities) and if the mobility of the charge carriers in the composite materials is high, the charge carriers will get separated very fast and collected at the electrodes.

2. Experimental details

The conducting polymers P3HT, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and CdSe/ZnS core shell QDs dispersed in toluene (5 mg/ml) were commercially procured from Sigma–Aldrich, USA. For the fabrication of solar cell, Indium tin oxide (ITO) coated glass having sheet resistance ∼15 Ω/sq was used as substrate and etched to obtain fine electrodes. The substrate so formed was then subsequently cleaned with isopropyl alcohol and acetone using ultrasonication. PEDOT:PSS was spin coated on the ITO substrate as hole transporting layer (HTL). The spin rate was kept at 3500 rpm for the duration of 30 s. The sample was then annealed at 100 °C for half an hour to remove extra-unwanted water from the HTL. A solution of P3HT (20 mg/ml) was made in chlorobenzene. This solvent was selected because not only does P3HT have a high solubility in chlorobenzene but their solubility parameters also match (18 Mpa$^{1/2}$, 19.4 Mpa$^{1/2}$, respectively [17]). The solution was homogenized by ultrasonication for 2 h. The solution was then filtered using 0.25 μ Polytetrafluoroethylene syringe filter. Afterwards, P3HT solution was spin coated on the PEDOT:PSS layer keeping the spin rate as 2000 rpm for 30 s. This sample was then annealed for 20 min at a temperature of 100 °C to remove the remaining residual solvent.

Subsequently, CdSe/ZnS QD layer was coated over P3HT film using the technique, as described in our previous work [18]. We did not use spin coating to deposit the QD layer because P3HT has a good solubility in toluene (in which QDs are already dispersed) and there is a possibility that it would dissolve the lower lying P3HT layer. For coating the QD layer over P3HT film we took ethylene glycol in a Petri dish and poured a few drops of the QD solution over it. The solution spreads uniformly over highly viscous glycol and floats over glycol. As the solution dries up, a thin floating layer (film) of QDs was obtained. The P3HT coated substrate was then placed over the dried composite film for a minute. As the glycol surface is non-sticky the floating film adheres itself to the substrate and the required double layer structure was obtained.

The sample was then placed in a vacuum oven to achieve inter-diffusion process of QDs into the active layer (P3HT). Four samples were made simultaneously in order to examine the effect of annealing duration on inter-diffusion process. These samples were annealed for different durations, i.e., 5, 6 and 7 min at an optimized temperature of 120 °C [4]. This temperature is well above the T_g (67 °C) [19] but lower than T_m (216 °C) [20] of P3HT. A thin layer of LiF was then vacuum-evaporated on the QD film. The purpose of LiF buffer layer is to check the migration of Al atoms into the device. Finally, Al cathode was grown using vacuum evaporation at 10^{-6} torr. The steps for solar cell fabrication are shown in Fig. 1(a)–(g).

The corresponding energy level diagram for the solar cell is shown in Fig. 2. It is clear from this figure that the photo generated electrons in P3HT can favorably be transferred from the LUMO level to conduction band of CdSe QDs. Similarly, the holes generated in CdSe QDs can be easily transferred from its valence band to HOMO level of P3HT. The energy level diagram shows that electron transfer from P3HT to CdSe QDs through ZnS core shell is also favorable.

The current density–voltage characteristics (*J*–*V*) of the solar cells were measured by Keithley Source Meter (SMU 2400). A 300 W Osram light source was used to illuminate the cell. The intensity of the light falling on the solar cell samples was measured by a lux meter and found to be 56,000 lux. The input power (P_{IN}) from the sun lamp was calculated to be 8.19 mW/cm^2, using the data of Dobrzański et al. [23]. For Scanning Electron Microscope (SEM), absorption and PL measurements, we made the same structure described above but here the glass substrate was taken instead of ITO. The thickness of the PEDOT:PSS, P3HT and QD layer as measured by a talystep was found to be 100 nm, 200 nm, and 80 nm, respectively with in 10%.

The SEM measurements were made for P3HT–QD films before and after annealing using Zeiss EVO MA 15. The absorption and PL spectra of the samples were measured using Shimadzu UV–Vis Spectrophotometer model UV 2450 and Shimadzu Spectrofluorophotometer model RF 5301 PC, respectively. All the measurements were made in air at room temperature without any device encapsulation.

3. Results and discussion

The typical micrographs of the bilayer P3HT–QD film are shown in Fig. 3(a) and (b) before and after annealing, respectively. The annealing is done in vacuum at 120 °C for 7 min (this is the optimum annealing temperature and duration for obtaining highest value of short circuit

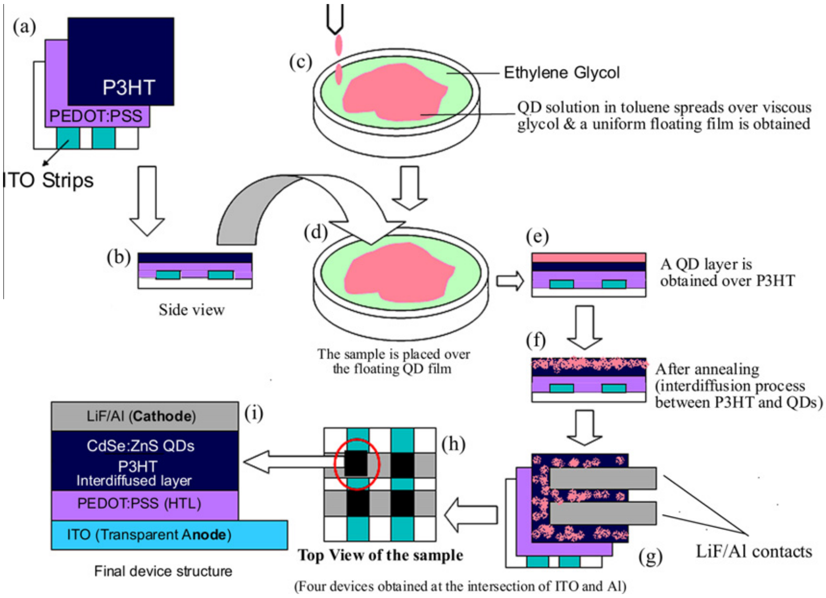


Fig. 1. Fabrication steps and schematics for the layer arrangement of the solar cell.

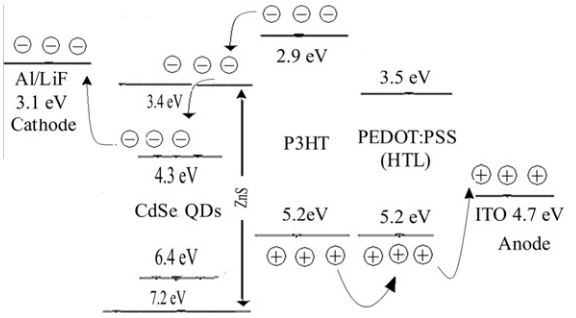


Fig. 2. Energy level diagram for the solar cell [21,22].

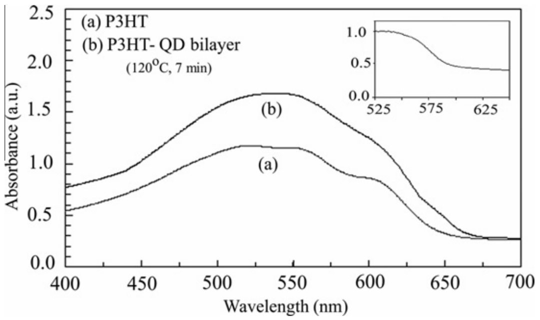


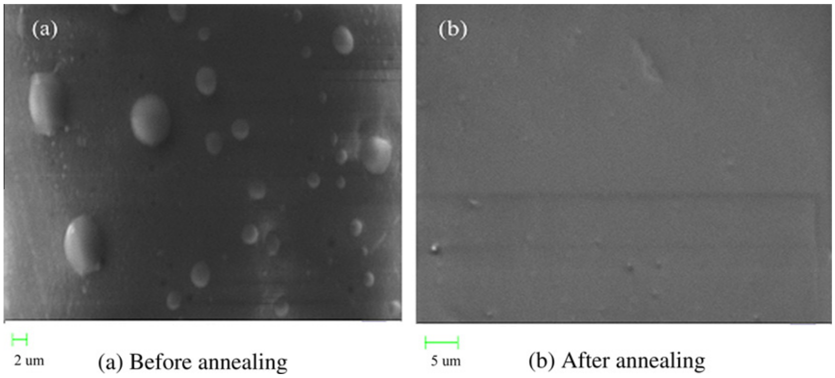
Fig. 4. Absorption spectra of P3HT–QD bilayer structure. Inset shows the normalized absorption spectrum of QDs.

current from the illuminated sample). From Fig. 3(a) it is found that QDs are deposited on the P3HT film with an average cluster size of ~2μm. However, after annealing (Fig. 3(b)), QDs are observed to be diffused into the polymer layer. The morphology of the films was also found to be very smooth ensuring that an intermingled BHJ structure of P3HT and QDs is formed. It may be mentioned that mere smoothness of the P3HT–QD surface is not a strong evidence for diffusion of QDs into the P3HT layer. This must be confirmed by PL measurements, which should show quenching of PL emission from P3HT, as the transfer of electrons from P3HT to QDs increases due to inter diffusion. This has been shown in Fig. 5 later.

The optical absorption spectrum of the optimally annealed P3HT is shown in Fig. 4 in the wavelength range 400–700 nm. It is found that the absorption spectrum is quite broad in the wavelength range 475–625 nm making the polymer highly suitable for the application in PV devices. The absorption spectrum of optimally annealed bilayer film is also shown in the same figure. The presence of QDs increases the absorption significantly but no shift in the absorption peak is observed. The optical absorption spectrum of the pristine P3HT–QDs bilayer was also measured. However, no measurable difference between annealed and un-annealed film was observed. Similar conclusion was also made by Drees et al. [13]. Both these factors are helpful for increasing the performance of the hybrid PV device. For the sake of comparison the absorption spectrum of the QDs film on a glass substrate is also shown in the inset of this figure. All the absorption values are normalized with respect to the absorption of P3HT film. The presence of an excitonic absorption edge at 550 nm is clearly seen in the normalized absorption spectrum of the QDs indicating the presence of QDs.

The PL measurements were also carried out in order to provide evidence for transfer of electrons from donor (P3HT) to acceptor (QDs) when BHJ is created with the help of inter-diffusion process. The PL spectrum for the bilayer P3HT–QDs films before and after annealing is shown in Fig. 5. The excitation wavelength used was 520 nm, which is appropriate for measuring the PL of P3HT. It is found that the PL of the optimally annealed film (7 min annealing duration) gets quenched by an order of magnitude. This ensures that there is a significant transfer of electrons from P3HT molecules to the QDs.

The *J*–*V* curves for the bilayer structures with and without annealing are shown in Fig. 6. It is found that the solar cell parameters such as open circuit voltage (V_{OC}), short circuit current (J_{SC}), maximum output power (P_{MAX}), fill factor ($FF = P_{MAX}/V_{OC}{*}J_{SC}$) and $PCE = P_{MAX}/P_{IN}$ are best for the solar cell annealed for 7 min. The cell parameters calculated for different annealing durations are summarized in Table 1. Annealing more than 7 min drastically deteriorates the film and hence the device performance. However, the effect of annealing on the open circuit voltage is not significant. It may be mentioned that the thickness of the active layer is very crucial. In the present case the thickness of P3HT layer is kept at ~200 nm. If the thickness is



(a) Before annealing (b) After annealing

Fig. 3. (a) and (b) SEM micrographs for the bilayer P3HT–QDs structure.

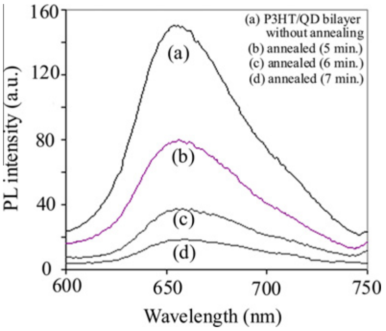


Fig. 5. Photoluminescence spectra for the P3HT–QD bilayer structure showing the effect of annealing.

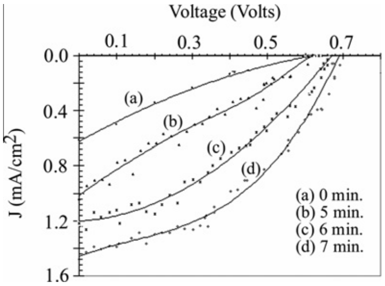


Fig. 6. *J*–*V* characteristics for the solar cells fabricated using annealed bilayer P3HT–QD technique.

Table 1
Variation of bilayer solar cell parameters with annealing duration. (The incident light is from a broadband white light source with an irradiance of 8.19 mW/cm^2.)

Annealing duration (min)	V_{OC} (Volts)	J_{SC} (mA/cm^2)	P_{MAX} (mW/cm^2)	FF	PCE (%)
0	0.59	0.616	0.071	0.20	0.8
5	0.61	1.04	0.186	0.29	2.1
6	0.63	1.22	0.295	0.38	3.6
7	0.62	1.48	0.423	0.45	5.1

lower, i.e., 100 nm several pinholes and micro cracks are formed resulting in a very low FF. On the other hand if the thickness is large, i.e., ∼300 nm the series resistance of the device increases resulting in lowering of the short circuit current.

4. Conclusion

It can be concluded that while in principle highly efficient BHJ solar cells can be fabricated by processing donors and acceptors from a common organic solvent, finding the proper processing conditions and compatible organic semiconductors to form an efficient BHJ can be rather difficult. For an OPV device, it is advantageous to use hybrid organic inorganic QD structure such as P3HT–CdSe QD structure and produce BHJ using inter thermal diffusion at a temperature which is higher than the T_g but lower than that of T_m. Using such a PV device and a broadband white light source with an irradiance of 8.19 mW/cm^2, we have been able to achieve a solar cell PCE of ∼5%. Attempts will be made to further improve the PCE by adding single walled carbon nanotubes in the composite along with a suitable linker.

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