Characterization of P3HT:PCBM:CdSe hybrid solar cells

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Abstract

We have investigated the effect of adding CdSe quantum dots (QDs) with their hexadecylamine (HDA) ligands coating in ITO/SPT/P3HT:PCBM/Al bulk heterojunction (BHJ) organic photovoltaic cells (OPV). At first, we found that the optimal thermal treatment was a post cathode deposition annealing, due to an effective surface area 10.8% larger compared to a pre-cathode thermal treatment. Absorbance spectra for hybrid cells with incorporated QDs diameters ranging from 2.2 nm to 6.3 nm show the largest absorbance for 3.3 nm QD diameter. The 3.3 nm QD also gives the lowest power performance. We explained the general degraded performance as an effect of the HDA ligands coating around QDs. Finally, in order to track the lateral inhomogeneity of the final device, we have mapped the I-V over the entire surface cell (2 cm x 2 cm) with a definition of 200 pts x 200 pts.

Keywords: Organic photovoltaic cell (OPV); Hybrid photovoltaic cells (HPV); Bulk heterojunction (BHJ); Quantum dots (QD); I-V mapping

1. Introduction

Photovoltaic cells based on organic semiconductors have attracted a lot of interest due to their potentially low production cost and flexible nature. Most of the research have been dedicated so far to the improvement of the power conversion efficiency (PCE) that is now approaching 8%, i.e. quite close to the 10% considered as the threshold limit for commercialization [1]. Various strategies have been used to improve the PCE of OPV cells, including the tandem architecture [2], the inverted architecture [3],...
thermal treatment to shape the morphology of the bulk heterojunction [4], adding additional photo-absorber such as quantum dots (QD) [5], etc.

Nevertheless, other issues than the ultimate PCE deserve attention for a commercially viable OPV product, for example the homogeneity of the photovoltaic performances over large area (i.e. dozens of cm² instead of mm²) or the degradation and the lifetime of the cell.

In this study, we have used the most prominent photoactive polymer blend in OPVs (i.e. P3HT:PCBM) to investigate:

- the optimum thermal treatment. What thermal treatment induce what change in the performance of the cell (J_{sc} or V_{oc}) and why? This issue is still much debated in the literature [6].
- the effect of adding CdSe quantum dots in the photoactive blend. Is the absorption improved as expected and what is the result on the PCE?
- the 2D homogeneity. Is the performance of the cell, prepared by spin-coating, homogenous over at least 2 cm x 2 cm?

2. Experimental

2.1. Materials

The photoactive layer, a polymer-fullerene heterojunction, is based on high molecular weight, highly regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) in 2.2% in dichlorobenzene (DCB). The hole transport layer, a sulfonated polythiophene (SPT) solution, is based on poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) in 2% in butyl cellosolve/water. Both photoactive and conductive polymers were synthetized by Plextronics® (Plexcore® PV 1000, Aldrich). The surface of the cadmium selenide (CdSe) quantum dots (QDs) (Nanoco Lumidot™ CdSe-6, Aldrich) is stabilized with a hexadecylamine (HDA) ligands coating. The kit contains 6 solutions, in toluene at a concentration of 5 mg/ml, with various diameters ranging from 2.2 to 6.3 nm (2.2, 3.3, 4.2, 4.9, 6.3 nm). We used 20 mm x 20 mm x 1.1 mm glass substrates with 100 nm indium-tin oxide (ITO) with a measured sheet resistance of 18 Ω/sq.

2.2. Device fabrication

The handling of polymers and the mixing with quantum dot solutions were carried out in a flexible glove box filled with argon. Photoactive solution has been used either as received or with several dilutions of QDs (1:8, 1:4, 1:2 vol.). As the two organic solvents (DCB and toluene) are miscible, there is no issue about phase separation. Moreover, all the processing of polymers is done with yellow filter light under laminar air flow.

The architecture of organic and hybrid photovoltaic cells are the following: glass/ITO/SPT/P3HT:PCBM/Al and glass/ITO/SPT/P3HT:PCBM:CdSe/Al, respectively. Prior to deposition, substrates are successively cleaned with acetone and isopropyl alcohol in an ultrasonic bath. The hole transport layer is spin-coated onto the ITO coating at 6000 rpm for 40 seconds and then dried on a hot plate at 80°C for 60 seconds. The photoactive mixture, preheated at 60°C to be homogeneous, is spin-coated onto the SPT layer at 3000 rpm for 40 seconds as well. The aluminium cathode, with an active surface area of 3.2 cm², is deposited by thermal evaporation (2·10⁻⁶ mbar) using 99.5% Al pellets. The resulting thicknesses of each layer, as measured by atomic force microscopy [7], were: 50 nm for SPT, 100 nm for P3HT:PCBM and 500 nm for Al. Thermal treatments are detailed in §3.1.
2.3. I-V characterization and performances mapping

I-V characterization has been performed using a voltage-controlled Keithley 2400 sourcemeter with the four wires gathered into a shielded cable connected to a guard. We used a halogen white light illuminator (Schott KL 1500 LCD) with a measured peak emission at 590 nm. For I-V measurement, the illumination power density is 2mW/cm².

In order to track the lateral homogeneity of our photovoltaic devices, a homemade setup has been developed based on two 150 mm motorized stages (Thorlabs NRT 150 and APT controller) and a 0.5 mm diameter illumination beam, focused through a 40x objective. Typically, we take an I-V curve every 0.1 mm over the entire cell, i.e. a set of 200 x 200 I-V curves for which the photovoltaic parameters (FF, Pmax, Voc, Isc, Vm, Im) are calculated.

3. Results and discussion

3.1. Organic Photovoltaic cells (OPV) – Thermal treatments effects

The main purpose of the thermal treatment is to control the morphology of the phase separated bulk heterojunction [8]. Ideally, a generated exciton should never be farther to a p-n junction than the exciton diffusion length, i.e. typically 10nm for the P3HT:PCBM blend. An optimized thermal treatment allows for domain crystallization of this size. As a result, the number of collected charges is maximum, thus the short circuit current density Jsc is maximized. According to the literature, annealing at 150°C during 5 to 10 min gives the best results [9].

The thermal treatment can influence other parameters such as the active surface area of the cathode, which also affects the device performances. Fig. 1 shows the J-V characteristics obtained for different thermal treatments: without thermal treatment (a), with pre-cathode annealing only (b), with pre- and post- cathode annealing (c) and with post-cathode annealing only (d).

We then found that:

• The pre-cathode treatment acts to improve Jsc (from 0.11 mA/cm² to 0.25 mA/cm²), an indication of the expected morphology change in the bulk hetero-junction.

• A subsequent post cathode treatment, while keeping the improved Jsc, results in the increase of Voc, (from 0.26 V to 0.34 V) indicating a change in the electronic charge transfer state.

• When the thermal treatment is done only after the cathode deposition, we have an additional increase of both Jsc and Voc compared to any other type of thermal treatments.

AFM nanotopography measurement (Fig. 1) showed that the surface roughness of P3HT:PCBM layer was significantly decreased by the thermal treatment when it was performed before the cathode deposition. Table 1 summarizes the roughness parameters of the active layer before and after a pre-cathode annealing.

The roughness parameters show clearly the influence of the pre-cathode bake on the topography of the P3HT:PCBM layer. The RMS roughness (Rq) is divided by a factor of three and the skewness (Rsk) and Kurtosis (Rku) roughness show that the surface becomes almost flat with shallow hollows. Therefore, if the cathode is deposited onto this flatten surface, its active surface area is significantly reduced (i.e. 10.8%) with corresponding degraded final performances.

3.2. Hybrid Photovoltaic cells (HPV) – Quantum dots size effects
In other studies [10-12], CdSe quantum dots have been used as the electron acceptor in P3HT:CdSe bulk heterojunctions solar cells. For such applications, it is necessary to remove the grafted alky chains on QD (surfactant), in order to reduce the electron hopping distance. For example, using hexonic acid to significantly reduce the HDA (hexadecylamine) ligand coating, a PCE of 2% has been reported [10].

In this study, we have incorporated untreated (i.e, with HDA ligand coating) CdSe QD in P3HT:PCBM cells. We therefore do not use QD CdSe as the electron acceptor but, we hoped, as an additional photo-absorber that could improve the cell efficiency. As the energy band gap (E_g) is a function of the QD diameter, we can study the effect for various E_g.

![Before pre-cathode annealing, (a) and (d)](image)

![After pre-cathode after (b) and (c)](image)

Fig. 1. Effects of thermal treatments on J-V characteristics and topography of P3HT:PCBM bulk heterojunction: (a) Without thermal treatments, (b) With pre-cathode annealing only, (c) With pre- and post-cathode annealing, (d) With post-cathode annealing only, and AFM nanotopography of photoactive layer corresponding to each curve. The surface area is significantly decreased when the annealing is carried out before the cathode deposition.

Table 1. Roughness parameters of P3HT:PCBM before and after pre-cathode annealing, measured by AFM on 20 μm x 20 μm field of view.

|                      | \( R_q (\text{nm}) \) | \( R_a (\text{nm}) \) | \( R_{sk} (\text{nm}) \) | \( R_{ku} (\text{nm}) \) | \( R_{dr} \) \( \times 10^5 \) |
|----------------------|----------------------|----------------------|----------------------|----------------------|-----------------|
| Before pre-cathode bake | 10.20                | 8.03                 | -0.29                | 5.63                 | 1.48 \( \times 10^5 \) |
| After pre-cathode bake  | 3.72                 | 2.96                 | -0.07                | 3.10                 | 1.32 \( \times 10^5 \) |

*Surface: \( S=S_0(1+R_{dr}) \), where \( S_0 \) is the footprint surface.

Fig. 2a) shows the J-V spectra on hybrid P3HT:PCBM:CdSe QDs (dilution 1:8 solution volume) having the indicated diameters, ranging then from 2.2 nm to 6.3 nm. In order to analyze these J-V curves, we have measured the optical properties of the final cells, i.e. with the Al electrode. Fig 2b) shows the absorbance spectra \( A(\lambda) \) deduced from the reflectance spectra \( R(\lambda) \) with \( A(\lambda) =1-R(\lambda) \) as no light is transmitted through the aluminum film. We can see the increase of absorbance with the addition of QDs, and this holds more or less whatever the QD diameter and the wavelength. Surprisingly, absorbance...
increase does not show specific absorbance peaks at wavelength corresponding to the band gap energy. Fig 3a) shows the maximal power worked out the J-V curves and Fig. 3b) shows the absorbance values as a function of the QD diameters for 4 selected wavelength (450 nm, 550 nm, 650 nm and 750 nm).

It appears that to the highest absorption, through the entire spectrum, corresponds the lowest maximal power output. This is certainly due to the hexadecylamine (HDA) ligands coating around QDs. This coating is integrated during the synthesis in order to stabilize their surface and prevent any aggregation. Unfortunately, this coating acts as an insulator that traps the charges once they have been generated. As a result, PCE is decreased. The maximal power generated by the photovoltaic cell is inversely proportional to the absorption. What is more clearly observable at 650 nm. Moreover, the cell without any QDs shows the better results. This last one has only been diluted in toluene with the same ratio (1:8 vol.) than the hybrid cells. Toluene as co-solvent with DCB might change drying conditions and therefore the bulk heterojunction structure. The parameters of each cell are synthesized in the Table 2.

3.3. $P_{\text{max}}$ mapping

In order to track the lateral inhomogeneity of our devices, the I-V characteristics have been mapped using a home-made setup, over the entire surface area (3.7 cm$^2$) with a definition of 200 pts x 200 pts.
Unlike laser-based commercially available systems (Photoresponse Mapping from Newport®) that perform photocurrent measurements at a selected wavelength, our setup takes full I-V curves on each spot illuminated with white light.

Table 2. Photovoltaic parameters of P3HT:PCBM: CdSe hybrid solar cells.

| Quantum dots diameter (nm) | Open circuit voltage $V_{oc}$ (V) | Short circuit current density $J_{sc}$ (mA/cm²) | Maximal power $P_{max}$ (mW) | Fill factor FF (%) |
|---------------------------|---------------------------------|-------------------------------------|-----------------------------|------------------|
| 2.2 nm                    | 0.49                            | -0.36                               | 0.17                        | 45.2             |
| 2.5 nm                    | 0.53                            | -0.37                               | 0.16                        | 38.0             |
| 3.3 nm                    | 0.46                            | -0.41                               | 0.16                        | 38.8             |
| 4.2 nm                    | 0.53                            | -0.44                               | 0.22                        | 44.1             |
| 5.3 nm                    | 0.53                            | -0.44                               | 0.28                        | 55.6             |
| 6.3 nm                    | 0.53                            | -0.45                               | 0.31                        | 61.2             |
| None                      | 0.53                            | -0.45                               | 0.32                        | 63.0             |

The comparison between optical images and power ($P_{max}$) mapping results showed defects that are correlated, caused by thickness inhomogeneity, and other defects that cannot be detected optically (uncorrelated), caused by changes in the chemical and/or physical properties of the polymers. An example is shown in Fig. 4: (a) a local defect created during the spin-coating of the photoactive layer, forming a

![Optical Microscope](image1)

![Pmax Mapping](image2)

(a)

![Optical Microscope](image3)

![Pmax Mapping](image4)

(b)

Fig. 4. Comparisons between optical images (left) and maximal power mapping (right). (a) A defect created during the spin-coating of the active layer affects performances; the variation can be seen on the optical image and the mapping (correlated defect). (b) For the case of silver paint used for the bonding, performance is reduced, but the variation cannot be seen on the optical image (uncorrelated defect).
“comet” (shown with arrows in Fig. 4a), induces performances variations (b) an important lack of performance is detected right under the bonding area (0.1 mm copper wire bonded with silver painting on the Al cathode). This last type of defect is certainly caused by the solvent and reaction by-products during the drying of the silver painting, which induces the degradation of the polymers.

4. Conclusions

This study have demonstrated that for a P3HT:PCBM bulk heterojunction, the most suitable thermal treatment is done when only a post-cathode annealing is performed for 10 min at 150°C. In this case, the active surface area of the cathode is over 10% larger than when the annealing is performed before the cathode deposition.

Results obtained for a P3HT:PCBM: CdSe hybrid heterojunction showed that to achieve better performances, the HDA ligands coating must be removed or at least reduced to allow charge transfer between the QD and the acceptor polymer. This can be achieved by a hexanoic or oleic acidetching. A detailed study of the band structure would also be necessary to understand charge transfer between both donor and acceptor polymer as well as with the QDs.

The mapping setup enables the investigation of the influence of each step during the fabrication and reveals defects that would remain invisible with other techniques. It also enables the study of thickness versus performances. Indeed, by producing a cell with a gradient of thickness, typically with a relatively low rotational speed during the spin-coating, the mapping will reveal all the variations (i.e. FF, P<sub>max</sub>, V<sub>oc</sub>, I<sub>sc</sub>, V<sub>m</sub>, I<sub>m</sub>). Moreover, it could be used to study the structuration of the active layer and/or the electrodes.

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