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OPTICAL PROPERTY AND PHOTOELECTRICAL PERFORMANCE OF A LOW-BANDGAP CONDUCTING POLYMER INCORPORATED WITH QUANTUM DOTS USED FOR ORGANIC SOLAR CELLS

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Received 16 May 2015
Accepted for publication 25 June 2015
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Abstract. By using spin-coating technique, a low bandgap conjugated polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopen-ta-[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and its composite thin films have been prepared. The optical absorption and photoconductive properties with over a wide spectral range, from 350 to 950 nm, were characterized. The obtained results showed that PCPDTBT:10 wt.% CdSe composite is the most suitable for efficient light-harvesting in polymer-based photovoltaic cells. The photoelectrical conversion efficiency (PCE) of the device with a multilayer structure of ITO/PEDOT/PCPDTBT:CdSe/LiF/Al reached a value as large as 1.34% with an open-circuit voltage ($V_{oc}$) = 0.57 V, a short-circuit current density ($J_{sc}$) = 4.29 mA/cm$^2$, and a fill factor (FF) = 0.27. This suggests a useful application in further fabrication of quantum dots/polymers based solar cells.

Keywords: PCPDTBT:QDs, heterojunctions, photoelectrical property, organic solar cell (OSC).

I. INTRODUCTION

In the last decade, organic solar cells (OSC) based on organic and polymeric materials are increasingly interesting because of their reduced fabrication cost [1–3]. Some conjugated polymers such as poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV, $E_g$ = 2.3 eV [4]), poly(3-octylthiophene-2,5-diyl) (P3OT, $E_g$ = 2.1 eV [5] and poly(3-hexylthiophene) (P3HT, $E_g$ = 1.9 eV [6]) were the most studied. In comparison with silicon ($E_g$ = 1.1 eV), these organic semiconductors possess a larger energy bandgap, therefore their absorption spectra have a less overlap with the solar emission spectrum. That is why, the power conversion efficiency of solar cells based on organic materials is rather low. However, as compared to inorganic solar cells like Si-single crystalline cells, the production technology for either materials or devices of OSCs is much simpler. At present, in the quest for higher organic-solar-cell efficiency there are two main approaches: the first is to focus on the synthesis of new polymers in which the optical bandgap is engineered to improve the harvesting of light from the sun; and the second is to incorporate the...
nanocrystals into polymer matrices in order to take advantage of the absorbance of many polymers. Recently, a novel low-bandgap polythiophene–benzothiadiazole copolymer, poly-2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole), abbreviated to PCPDTBT has been produced and commercialized. A slightly different value of the bandgap of PCPDTBT was reported as $E_g = 1.46$ eV [7] or 1.40 eV [8]. This $E_g$ is much lower than that of the above-mentioned polymers. The molecular structure and bandgap diagram of PCPDTBT are shown in Fig. 1.

![Molecular structure of PCPDTBT](image1)

![Bandgap diagram of PCPDTBT](image2)

**Fig. 1.** The molecular structure (a) and schema of the bandgap of PCPDTBT (b) [8]

The reason why the efficiency of an organic solar cell until now is still low is usually attributed to the strong decay of the excitons which are generated in the donors/acceptors junctions owing to the illumination of solar radiation. The exciton decay can be diminished by the creation of either appropriate heterojunctions or nanocomposites. In the nanocomposite materials a luminous quenching effect (LQE) has been observed [7]. The stronger LQE, the better so-called charge separation occurs, i.e. generated electrons and holes faster move to opposite directions. It has been known that by embedding inorganic nanocrystalline oxides like TiO$_2$ nanoparticles (nc-TiO$_2$) into polymer matrices, one can enhance the efficiency and service duration of the organic devices. The embedded oxides can substantially influence both the electrical and optical properties of the polymer, for instance MEH-PPV + nc-TiO$_2$ composite thin films were studied as a photoactive material [8-9]. Thomas et al [10] and Liu [11] gave reviews on the recent progress on hybrid/composite photovoltaic systems of inorganic semiconductors and organic conducting polymers. Nanostructures and their influence on the photovoltaic performance of these hybrid materials have been analyzed. By using hybrid or nanocomposite materials for the photoactive layer, one can enhance the power conversion efficiency of composite-based OSC.

This work presents results of our recent research on the absorbance properties of nanocomposites served as the photoactive layer, namely PCPDTBT embedded with either CdS or CdSe quantum dots (PCPDTBT:CdS and PCPDTBT: CdSe). The performance of OSCs based on these nanocomposites is also presented.
II. EXPERIMENTAL

The CdS- and CdSe-QDs with 7 nm in size were synthesized using a method reported in [13] with a doubled concentration of precursors. Polymer PCPDTBTB with a 99.99% purity was provided by the Sigma Aldrich chemicals Ltd. The bulk donor–acceptor heterojunction solar cells were produced by spin coating. The detail of the fabrication method can be seen elsewhere [14]. To compare the photoactive behavior and the performance of the devices made from the pure PCPDTBTB and composites of PCPDTBTB:QDs abbreviated respectively to PQ1 and PQ2, for CdS- and CdSe-QD, PCPDTBTB and PQ thin films onto Sn-doped In$_2$O$_3$ (ITO) coated glass substrates were prepared by spin-coating method. The ITO substrates (150 nm in thickness and 15 Ω/□ in sheet resistance) of were ultrasonically cleaned in distilled water, followed by cleaning in ethanol and acetone. For improvement of the ITO contact, the ITO was coated with a 70 nm-thick layer of polyethylene dioxythiphene in poly(4-styrenesulfonate) (PEDOT:PSS/ITO). To deposit the active layers onto PEDOT:PSS/ITO, the PCPDTBTB solution was prepared by dissolving 10 mg of PCPDTBTB powders in 1 ml of chloroform. For the composites, the QDs were embedded in the PCPDTBTB solution according to a weight ratio QDs/polymer of 0.10 (i.e. 10 wt. %). This ratio, as reported in [15], is the optimal content for both the generation and separation of charges (electrons and holes) under illumination of solar energy radiation. To obtain a homogenous dispersion of QDs in the polymer, the solutions were well mixed together for 8 hours by using magnetic stirring. Further, these PCPDTBTB and PQ solutions were used for spin-coating onto the ITO substrates. The conditions for spin-coating were as follows: a delay time of 120 s, a rest time of 30s, a spin speed of 1500 rpm, and an acceleration of 500 rpm, and finally a drying time of 2 min. The thickness of the PCPDTBTB and PQs active layers was controlled at a value of 100 nm. The samples used for UV-Vis-NIR spectra measurements with a thickness of 200 nm were deposited onto Corning-7070 glass substrates. All the samples were put in a flow of dried gaseous nitrogen for 12 hours. As electrodes, a PEDOT:PSS/ITO film on one side and a LiF/Al bilayer contact on the other side were used. A 120 nm-thick LiF/Al electrode (shallow contact) was chosen instead of pure Al in order to ensure a good ohmic contact between the metal and the organic layer [16]. The LiF/Al electrode was successively evaporated in a vacuum of $1.33 \times 10^{-3}$ Pa, using a mask with windows of 2.5 mm × 3 mm in size. Therefore, the active area of the cell was 0.09 cm$^2$. By this way, three types of organic solar cells (OSC) with respective structures of ITO/PEDOT:PSS/PCPDTBTB/LiF/Al, ITO/PEDOT/PQ1/LiF/Al and ITO/PEDOT/PQ2/LiF/Al (respectively abbreviated to OSC-1, OSC-2 and OSC-3) were prepared, where the active layer of the OSC-1, OSC-2 and OSC-3, respectively is pure PCPDTBTB, PQ1 and PQ2 films. The design of those devices is presented in Fig. 1.

Absorption spectra of the samples were carried-out on a Jasco V-570 UV-Vis-Nir spectrometer. The performance of the OSCs was carried-out on an AutoLab-Potentiostat PGS-12 electro-chemical unit with an illumination power of 50 mW/cm$^2$ taken from “Sol 1A” Newport source which provides an energy spectrum similar to the solar one.

III. RESULTS AND DISCUSSION

III.1. Absorption spectra

Fig. 3 shows the absorbance ($\alpha$) spectra of pure PCPDTBTB, CdS and CdSe quantum dots solutions, respectively. The absorption spectra of QDs have only one peak at 480 nm for CdS and
Fig. 2. Schematic drawing of OSCs based on nanocomposite of PCPDTBT:QDs. Thickness of the PQ1 and PQ2 layers is of 100 nm, PEDOT:PSS layer – 70 nm, ITO layer – 150 nm and LiF/Al electrode – 120 nm.

605 nm for CdSe, whereas PCPDTBT have two peaks: one at 765 nm is much more intensive and another one at 400 nm is smaller. All these four broad spectra are in the solar radiation range, thus the combinations of PCPDTBT and both two QDs are suitable for use in Q-OSCs. However, the CdSe-QDs exhibit a better material for solar cell because its absorption spectra more overlap with the one of PCPDTBT (Fig. 3a). As compared to the solar spectrum (Fig. 3b) the PCPDTBT enables to collect about 64% of the available solar photon flux, whereas P3HT collects only 46%, as reported in [7].

Fig. 3. The absorbance spectra of CdS, CdSe and PCPDTBT solutions (a) and reference AM 1.5 solar spectrum (spectral irradiance of the sun on the earth’s surface under illumination at 45˚, AM: air mass [7]) (b).

Fig. 4 shows the absorbance spectra of PCPDTBT, PQ1 and PQ2 thin films. For both two polymeric composites (namely PQ1 and PQ2) the absorbance enhancement of samples was...
observed at red wavelengths. For PQ1 and PQ2 samples, the absorbance was much larger than that of the pure PCPDTBT. The highest absorbance at $\lambda = 760$ nm for PQ2, then a little lower absorbance at bright-red wavelengths for PQ1, and the lowest absorbance is of the pure polymer sample.

To compare the enhancement in absorbance between PQ1 and PQ2 composites relative to the pure polymer, one can introduce a relative enhancement coefficient ($\tau$) that is calculated by following equation.

$$\tau = \frac{\alpha_c - \alpha_p}{\alpha_c}$$

where $\alpha_p$ and $\alpha_c$ are the absorbance peaks of polymers and composites, respectively. From Fig. 4 and by applying Eq. (1), $\tau$ of PQ1 and PQ2 samples was found to be of 35.5% and 43.1%, respectively. The result of the calculation shows that the absorbance of PQ2 increased about 20% in comparison with the PQ1 sample. This indicates that the PQ2 film is a better candidate for the photoactive layer in Q-OSCs. In Fig. 4, there is observed a blue shift (9.4 nm) of the absorbance peak of the composites towards the pure PCPDTBT. The obtained result is similar to the one that was reported in [16–18]. This effect was explained due to a reduction of the conjugation chain length in conducting polymers by embedding of SiO$_2$ nanoparticles in PPV [18] or TiO$_2$ in MEH-PPV [16].

The absorbance of the PQ1 and PQ2 samples is stronger than the one of the pure PCPDTBT. Similar results obtained for P3HT incorporated with CdSe-QDs were reported in [8] and were explained due to the forming of the QDs/conducting polymer blend (Fig. 5). Due to the energy level offset between the polymers and the QDs, in both cases QDs act as electron acceptors and polymers as hole acceptors.
As reported in [19, 20], CdSe-QDs embedded in a hole-conducting polymer like MEH-PPV have formed heterojunctions between the QDs and conjugated polymer. When QDs were excited by photon energy larger than $E_g$ of QDs, the photogenerated holes are injected into the polymer and collected via a charge-transport layer to an electrode. In our experiments PCPDTBT used is an electron-conducting polymer, under the illumination the photogenerated electrons in the polymer are injected into QDs and collected via PEDOT-PSS (a hole-conducting) to the ITO electrode. On the opposite direction, holes move via LiF to the Al electrode.

### III.2. Photoelectrical conversion performance

Characterization of devices performance parameters such as open voltage ($V_{oc}$), short circuit current density ($J_{sc}$) and fill factor ($FF$) was carried out on the Auto-Lab. potentiostat using cyclic voltammetry ($CV$) measurements in both the dark and illumination. The maximum value of power density $P_{max}$ is obtained when the product between current-density and voltage is maximized:

$$P_{max} = (J \times V)_{max}$$

with $(J \times V)_{max}$ being maximum obtained power density.

The power conversion efficiency ($PCE$) of the solar cell is then defined as the ratio between the maximum power produced by the solar cell $P_{max}$ and the incident power density ($P_{in}$) as follows:

$$PCE = \frac{P_{max}}{P_{in}} = \frac{(J \times V)_{max}}{P_{in}} = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}}$$

where $FF$ is defined as:

$$FF = \frac{(J \times V)_{max}}{J_{sc} \times V_{oc}}$$

$FF$ is determined by the charge carriers reaching the electrodes, when the built-in field is lowered toward the open circuit voltage.

The current-voltage (I-V) characteristics measured under illumination of a density of the illuminating power $P_{in} = 50$ mW/cm$^2$ for three devices OSC-1, OSC-2 and OSC-3 were shown in Fig. 6. The arrows in this figure show the values of $J_{sc}$ and $V_{oc}$. By applying Eqs. (2)–(4) one can determine FF, consequently $PCE$. The obtained results are listed in Table 1. The PCPDTBT:CdSe (i.e. OSC-3) cell exhibited a PCE of 1.34% with an open-circuit voltage ($V_{oc}$) = 0.57 V, a short-circuit current density ($J_{sc}$) = 4.29 mA/cm$^2$, and a fill factor ($FF$) = 0.27. This demonstrates a best interconnection in the acceptor material of the CdSe containing cell, allowing to enhance the high-efficient electron confinement, consequently to increase the photon conversion efficiency.
absorbance. The other cells (OSC-1 and OSC-2) exhibited a poorer photovoltaic performance: the PCE of OSC-1 and OSC-2 reached a value as large as 0.36% and 0.65%, respectively (see Table 1).

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<th>Polymer</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
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<td>PCPDTBT</td>
<td>2.03</td>
<td>0.44</td>
<td>0.21</td>
<td>0.36</td>
</tr>
<tr>
<td>PCPDTBT:CdS</td>
<td>3.63</td>
<td>0.42</td>
<td>0.23</td>
<td>0.65</td>
</tr>
<tr>
<td>PCPDTBT:CdSe</td>
<td>4.29</td>
<td>0.57</td>
<td>0.27</td>
<td>1.34</td>
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From Table 1 one can see that the suitable configuration of conducting polymer and QDs (PCPDTBT:CdSe) resulted in a considerably large photoelectrical conversion efficiency, namely $PCE = 1.34\%$. Since QDs have very small particle size, they possess a special property so-called "multiple exciton generation" (MEG). Upon photoexcitation of the QDs, the photogenerated holes are injected into the PCPDTBT. The electrons remain in the CdSe-QDs and are collected through diffusion and percolation in the polymer phase to an electrical contact to the device network. Therefore, the PCE of a Q-OSC could be much improved, thus the MEG in QDs could make a large impact on solar energy technologies [21]. Recently, the improvement in the performance and stability of Q-OSCs has been achieved through band alignment engineering [22].

IV. CONCLUSION

Optical property of a low-bandgap conducting polymer PCPDTBT incorporated with CdS- and CdSe-QDs thin films were characterized by using UV-Vis-NIR absorption spectra measurements with over a wide spectral range, from 350 to 950 nm. The obtained results showed that in this spectral range the absorbance of the PCPDTBT:CdSe film is the largest. With embedding 10 wt.% CdSe, PCPDTBT:CdSe composite is most suitable for efficient light harvesting in polymer-based photovoltaic cells. The device with a multilayer structure of ITO/PEDOT/ PCPDTBT:CdSe/LiF/Al possesses a PCE of 1.34% with an open-circuit voltage ($V_{oc}$) = 0.57 V, a short-circuit current density ($J_{sc}$) = 4.29 mA/cm$^2$, and a fill factor (FF) = 0.27.

ACKNOWLEDGMENT

This research was funded by the Vietnam National Foundation for Science and Technology (NAFOSTED) under grant number 103.02-2013.39.

REFERENCES


