Optical Property and Photoelectrical Performance of a Low-bandgap Conducting Polymer Incorporated with Quantum Dots Used For Organic Solar Cells

Tran Thi Thao[1], Tran Quang Trung[2], Vo-Van Truong[3], and Nguyen Nang Dinh[1]

1- University of Engineering and Technology, VNU in Hanoi, No. 144 Xuan Thuy Road, Cau Giay District, Hanoi

2- University of Natural Science, VNU in Ho Chi Minh City, 227 Nguyen Van Cu Road, District 5, Ho Chi Minh City

3- Department of Physics, Concordia University, 1455 De Maisonneuve Boulevard W, Montreal, QC, Canada

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 (Voc) = 0.57 V, a short-circuit current density (Jsc) = 4.29 mA/cm2, 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).

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, Eg = 2.3 eV [4]), poly(3-octylthiophene-2,5-diyl) (P3OT, Eg = 2.1 eV [5] and poly(3-hexylthiophene) (P3HT, Eg = 1.9 eV [6]) were the most studied. In comparison with silicon (Eg = 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′′]dithio-phene)-alt-4,7-(2,1,3-benzothiadiazole), abbreviated to PCPDTBT has been produced and commercialized. The bandgap of PCPDTBT is about 1.40 eV [7] that is much lower than that of the above-mentioned polymers. The molecular structure and bandgap diagram of PCPDT
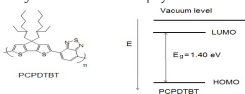

Fig.1. The molecular structure (a) and schema of the bandgap of PCPDTBT (b).

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.

Methods

The CdS- and CdSe-QDs with 7 nm in size were dissolved in PCPDTBTB polymer to make Polymer:QDs thin films (PQ1 and PQ2 for CdS- and CdSe-QD). PQ1 and PQ2 were prepared by spin-coating method on PEDOT:PSS/ITO substrates.The LiF/Al electrode was successively evaporated in a vacuum of 1.33×10-3 Pa. By this way, three types of organic solar cells (OSC) with respective structures of ITO/PEDOT:PSS/PCPDTBT/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 PCPDTBT, PQ1 and PQ2.

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 electrochemical 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.

Fig 2. (a)- The spin-coating bethod; (b)- the sputtering method; (c)- the Organic Solar Cell

Results

Absorption spectra

Figure 3 shows the absorbance spectra of pure PCPDTBT, CdS and CdSe quantum dots solutions. The absorption spectra of QDs have only one peak at 480 nm for CdS and 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. 4) the PCPDTBT enables to collect about 64% of the available solar photon flux, whereas P3HT collects only 46%, as reported in [7].
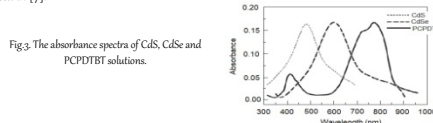

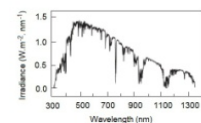Fig.3. The absorbance spectra of CdS, CdSe and PCPDTBT solutions.

Fig 4. The reference AM 1.5 solar spectrum (spectral irradiance of the sun on the earth's surface under illumination at 45°, AM: air mass.

Figure 5 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 λ= 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.
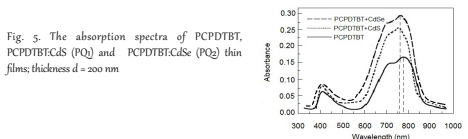

Fig. 5. The absorption spectra of PCPDTBT, PCPDTBT:CdS (PQ1) and PCPDTBT:CdSe (PQ2) thin films; thickness d = 200 nm
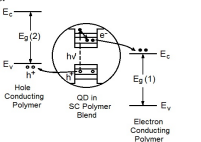

Fig. 6. The band structure diagram of the HOMO and LUMO energies of polymers relative to the band structure of quantum dots.

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. 5, 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 [15, 17]. This effect was explained due to a reduction of the conjugation chain length in conducting polymers by embedding of SiO2 nanoparticles in PPV [17] or TiO2 in MEH-PPV [15].

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 [18] and were explained due to the forming of the QDs/conducting polymer blend (Fig. 6). 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 Eg of QDs, the photogenerated holes are injected into the polymer and collected via a charge-transport layer to an electrode.

Photoelectrical conversion performance

Characterization of devices performance parameters such as open voltage (Voc), short circuit current density (Jsc) 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 Pmax is obtained when the product between current-density and voltage is maximized: $P_{max} = (J \times V)_{max}$

The power conversion efficiency (PCE) of the solar cell is then defined as the ratio between the maximum power produced by the solar cell Pmax and the incident power density (Pin) as follows:

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

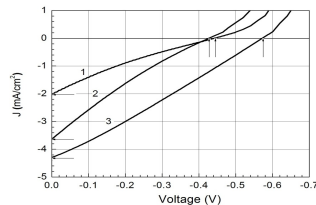where FF is defined as: $FF = (J \times V)_{max} / (J_{sc} \times V_{oc})$

Fig. 7. Current density-voltage (J-V) characteristics of the cells prepared from a pure PCPDTBT (1), a blend of P3HT:CdS (2) and PCPDTBT:CdSe (3) under illumination with Pin = 50 mA/cm2.

Table 1. Comparison of the photovoltaic devices performance properties based on PCPDTBT and PCPDTBT:QDs systems.

Polymer	J_{sc}[mA/cm−2]	V_{oc} [V]	FF	PCE [%]
PCPDTBT	2.03	0.44	0.21	0.36
PCPDTBT:CdS	3.63	0.42	0.23	0.65
PCPDTBT:CdS	4.29	0.57	0.27	1.34

The current-voltage (I-V) characteristics measured under illumination of a density of the illuminating power Pin = 50 mW/cm2 for three devices OSC-1, OSC-2 and OSC-3 were shown in Fig. 7. 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 (Voc) = 0.57 V, a short-circuit current density (Jsc) = 4.29 mA/cm2, 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 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).

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].

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 (Voc) = 0.57 V, a short-circuit current density (Jsc) = 4.29 mA/cm2, and a fill factor (FF) = 0.27.

Acknowledgment

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