Characterization of Organic Solar Cells Made from Hybrid Photoactive Materials of P3HT:PCBM/nc-TiO$_2$

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Abstract: Nanorod-like TiO$_2$ was grown on Ti wafers by annealing at 700°C for 1.5h. Hybrid Organic Solar Cells (HOSC) were then prepared by using a nano hybrid material of P3HT:PCBM/nc-TiO$_2$. The HOSC have the laminar structure of Al/P3HT:PCBM/TiO$_2$/Ti, where P3HT:PCBM were made by spincoating. Under illumination of the standard light wavelength (λ = 470 nm), the polymer luminescence quenching was observed at the heterojunctions, resulting in the charge separation. With an illumination power of 56 mW/cm^2, a best hybrid solar cell exhibited an open circuit voltage of 0.60 V, short cut current density of 4.60 mA/cm^2, fill factor of 0.54 and photoelectrical conversion efficiency of 2.6 %. This suggests a useful application for fabricating "reverse" OSCs, where the illumination light goes-in through the windows of Al-electrode cathode, instead of the indium tin oxide (ITO). For these devices, the Ohmic contact of wires to metallic Ti-substrates can be made much better than to ITO electrode.

Keywords: Organic Solar cell (OSC); nanorod-like TiO$_2$, P3HT:PCBM/nc-TiO$_2$ heterojunctions; polymer quenching.

1. Introduction

Recently, there has been increasing interest in both theoretical and experimental works on conducting polymers and polymer-based devices, due to their potential application in optoelectronics, organic light emitting diodes (OLED), organic solar cells (OSC), etc [1−4]. Similar to inorganic semiconductors, from the viewpoint of energy bandgap, semiconducting polymers also have a bandgap – the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). When sufficient energy is applied to a semiconducting polymer, electrons from the HOMO level (valence band) are excited to the LUMO level (conduction band). This excitation process leaves holes in the valence band, and thus creates "electron-hole-pairs"

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(EHPs). When these EHPs are in intimate contact (i.e., the electrons and holes have not dissociated) they are termed "excitons". In presence of an external electric field, the electron and the hole will migrate (in opposite directions) in the conduction and valence bands, respectively. It is well-known that inorganic semiconductors when reduced to the nanometer regime possess characteristics between the classic bulk and molecular descriptions, exhibiting properties of quantum confinement. Thus, adding metallic, semiconducting, and dielectric nanocrystals into polymer matrices enables the enhancement of efficiency and service duration of the devices [5, 6]. The inorganic additives usually were nanoparticles. The influence of nanocrystalline oxides on the properties of semiconducting polymers has been largely investigated by many groups [7,8]. It has been found that nanostructured composites and nanohybrid layers or heterojunctions can be applied to a variety of practical purposes.

It is seen that to develop viable devices such as organic solar cells (OSC) there are two approaches have been developed [9]: (i) the donor–acceptor bilayer, commonly achieved by vacuum deposition of molecular components, and (ii) the so-called bulk heterojunction (BHJ), consisting of a bicontinuous composite of donor and acceptor phases. The BHJ solar cells based on poly(3-hexylthiophene) (P3HT) with an energy bandgap of 1.9 eV [10] and the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) - that are currently considered to be the ideal acceptors for OSC - are most investigated. PCBM have an energetically deeplying LUMO [11], which endows the molecule with a very high electron affinity relative to the numerous potential organic donors like P3HT. However to improve photoelectrical conversion efficiency in such BHJ solar cells, the following difficult problems can be dealt with: the charge separation efficiency, electronic interactions between the polymeric donors and the fullerene acceptors, Ohmic contact between wires and electrodes, etc.

This work presents recent results of our research on nanohybrid materials used for OSCs. Those are BHJ of a mixture of P3HT:PCBM and nanorod-like TiO_2 (nc-TiO_2) grown directly from metallic Ti wafers.

2. Experimental

To grow nanorod-like TiO_2, a Ti wafer with a size of 2 mm in thickness, 20 mm in width and 25 mm in length were carefully polished using synthetic diamond paste. The polished surface of Ti was ultrasonically cleaned in distilled water, followed by washing in ethylene and acetone. Then the dried Ti wafers were put in a furnace, whose temperature profile could be controlled automatically. The annealing temperature profile is as follows: from room temperature, the furnace was heating up to $700^{o}C$, kept at this temperature with duration of 1.5 h, then followed by cooling down to room temperature during three hours. A mixture of P3HT and PCBM (abbreviated to MPL) was used for the photoactive layer. For this, the MPL mixture was prepared with a volume ratio of P3HT: PCBM equal to 1:1, then dissolved in chlorobenzene with a concentration of 1wt% and stirred at $50^{o}C$ for 5 h. The MPL solution was kept at $20^{o}C$ in a dark bottle which was placed in a glove-box until use. To get hybrid heterojunctions of MPL/nc-TiO_2/Ti the MPL solution was coated onto nc-TiO_2 layer by spincoating, followed by annealing at $120^{o}C$ in a low vacuum (the pressure ~ 10^{-2} Pa). The coating process was carefully carried-out in order that a thin layer (~ 70 nm) of MPL would be left on the nc-TiO_2 surface.

Then a 100 nm-thick Al-electrode onto MPL/nc-TiO$_2$/Ti was thermally evaporated in vacuum of 1.33×10^{-3} Pa, using a mask with windows of 4 mm × 5 mm in size for each. Therefore, the active area of a cell is 0.20 cm^2. By this way, the hybrid organic solar cells (HOSC) having the structure of Al/MPL/nc-TiO$_2$/Ti were prepared, as shown in Fig. 1.
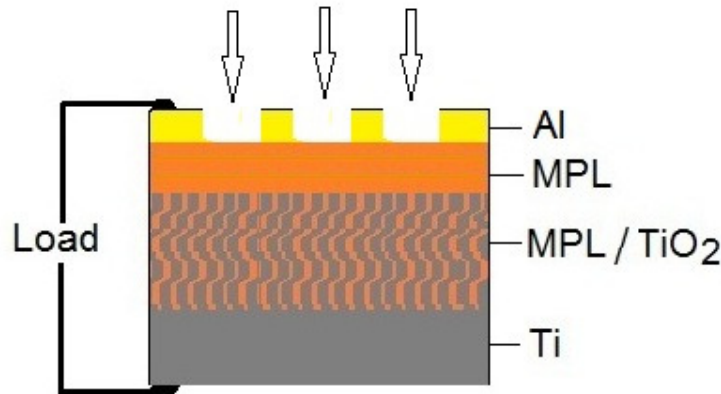

Fig. 1. Schematic drawing of a HOSC. Thickness of nc-TiO$_2$ sensitized by MPL (MPL/TiO$_2$) layer is ~ 200 nm, the MPL layer – 70 nm and the aluminum electrode – 100 nm.

Crystalline structure and surface morphology of TiO$_2$ were checked, respectively on a "Brucker D8-Advance" diffractometer using filtered Cu Kα radiation and on a "Hitachi S-4800" Field Emission Scanning Electron Microscope (FE-SEM) using a high Dc-voltage of 5 kV. The performance of the HOSCs was carried-out on a AutoLab-Potentiostat PGS-12 electrochemical unit with an illumination power of 56 mW/cm^2 taken from "Sol 1A" Newport source which provides an energy spectrum similar to solar one. Absorption spectra of the samples were carried-out on a Jasco V-570 UV-Vis-Nir spectrometer. Quenching effect of the hybrid layer was studied by photoluminescence spectra (PL) on a FLuoroMax-4 spectrofluorometer, using radiation of Xe-lamp for excitation.

3. Results and discussion

The XRD patterns of the annealed Ti-wafer are similar to the reported in [12] result that showed an average value of the TiO$_2$ particles equal to about 40 nm. The surface morphology of an annealed sample is revealed by FE-SEM micrograhps (Fig. 2). This figure shows the porous titanium surface layers, where Ti oxides were grown in form of nanorods. This image reflects such a high resolution of the FE-SEM, that from them one can determine approximately both the size on the surface and the depth of TiO$_2$ nanorods grown from the Ti-wafer. The result showed that TiO$_2$ rods have a width of ~ 50 nm and a length of from 100 to 200 nm. Moreover, a large number of the rods have orientation close to the vertical direction (Fig. 2).

In Fig. 3 there are presented two spectra of the same MPL sample. Left side curve is the UV-Vis spectrum with 4 peaks; among them three peaks in the visible range belong to P3HT and one peak in

ultra-violet (330 nm) is of the PCBM [13]. Right side curve is the PL spectrum with an excitation wavelength λ = 325 nm. With such a short wavelength excitation the MPL emitted one strong broad peak at 720 nm and less intensive peak at 670 nm. According to Ulum et al [14] the PL spectrum of P3HT has two transitions, namely 0-0 and 0-1, resulting in peaks at 670 nm and 720 nm, respectively. A rather weak peak at a short wavelength (370 nm) belongs to PCBM.
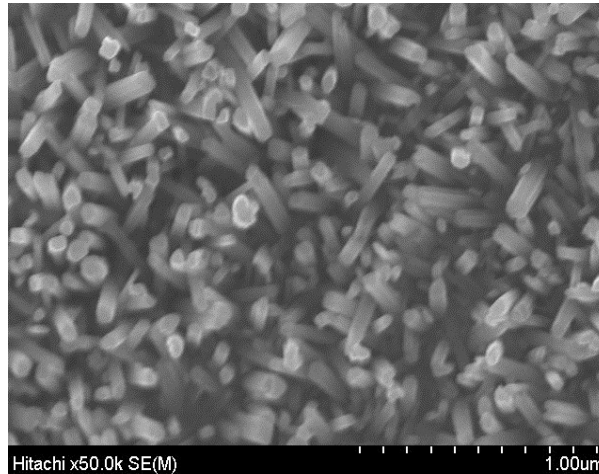

Fig. 2. A FE-SEM micrograph of the Ti-wafer annealed at 700°C for 1.5 h.

In Fig. 4 the PL spectra for the MPL and the MPL/nc-TiO$_2$ hybrid films with excitation wavelength of 470 nm are plotted. In this case, the clear MPL luminescence quenching was observed at red wavelengths. For MPL sample, the photoemission has a broad peak at 720 nm, whereas for the hybrid sample, containing numerous nano-heterojunctions of MPL/ nc-TiO$_2$, the photoemission peak shifted ~ 25 nm toward the blue wavelength range. It is a blue shift that was observed for the hybrid sample of poly(para-phenylene vinylene) (PPV)/nc-SiO$_2$ [15] and the authors explained this due to a reduction in the polymer conjugation chain length, when nanoparticle of SiO$_2$ were embedded in the polymer. In our experiments, the MPL polymer was partially broken by the TiO$_2$ nanorods.
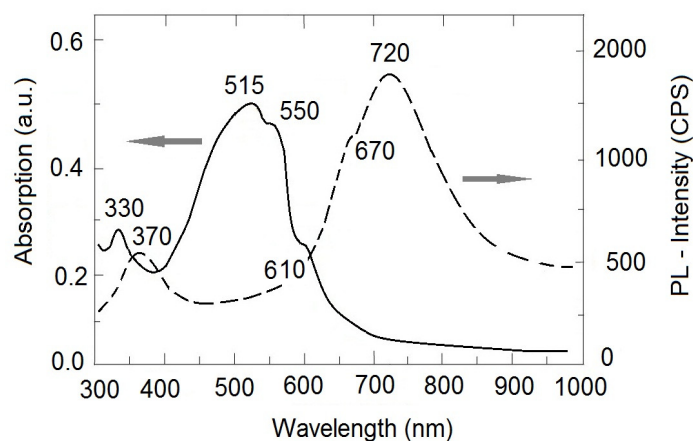

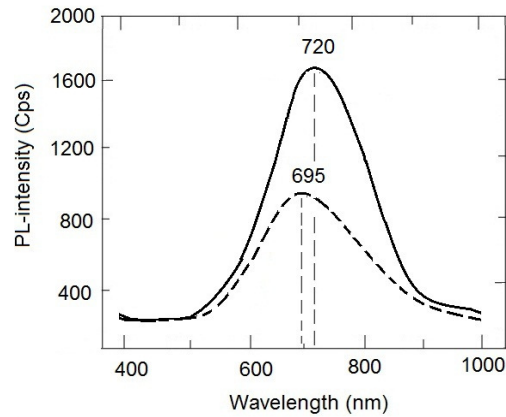Fig. 3. Absorption (left curve) and PL spectra (right curve) of a MPL sample.

Fig. 4. PL spectora of a MPL (solid curve) and MPL/nc-TiO$_2$ (dash curve).

As seen in [3], for a composite, in the presence of rod-like TiO$_2$ nanocrystals, PPV quenching of fluorescence is significantly strong. This phenomenon was explained by the transfer of the photogenerated electrons to the TiO$_2$. Thus, the fluorescence quenching of PPV is the consequence of the charge-separation at interfaces of TiO$_2$/PPV. This is a specific property that is desired for designing a simple, but prospective organic solar cell. The similar quenching effect that occurred in the P3HT:PCBM/nc-TiO$_2$ can be explained by use of the energy bandgap structure of the heterojunctions relative to a large bandgap (Eg) of TiO$_2$ [16] (Fig. 5).

The light (excited photons) of an energy larger than Eg of P3HT go through the windows of Al-electrode, then excite electrons from the HOMO level of P3HT. These electrons jump to the LUMO, generating holes (or creating excitons in P3HT). In case of a pure P3HT (i.e. there are neither PCBM nor nc-TiO$_2$ for a short life-time these excitons decay, emitting luminous photons. However, in the hybrid materials, due to the lower barriers between P3HT, PCBM and TiO$_2$, the generated electrons move to the Ti/TiO$_2$ (namely cathode) and holes move to opposite side – Al electrode (anode). By this way, one can have a voltage between two electrodes.
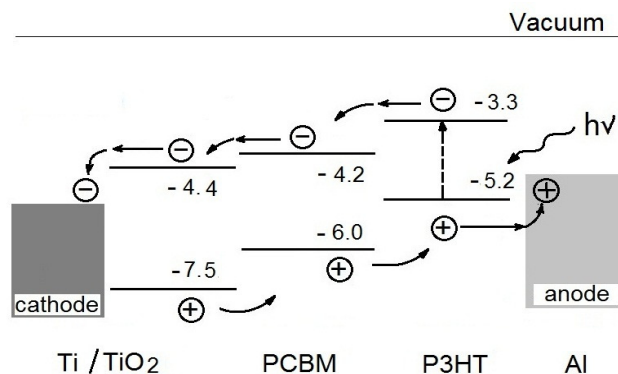

Fig. 5. Band structure diagram illustrating the HOMO and LUMO energies of P3HT and PCBM relative to the band structure of TiO$_2$. Energy values are reported as absolute values relative to a vacuum.

The performance of the HOSC is revealed by a cyclic voltammetry (CV) measurement in both the dark and the illuminated light. The obtained CV curves just exhibited the current-voltage (I-V) characteristics of the device which are shown in Fig. 6. In this figure the light-gray rectangle illustrates afill factor (FF) that can be determined by formula:

$$FF = \frac{(J \times V)max}{Jsc \times Voc} \qquad (1)$$

where Jsc is the density of short cut current, Voc - open circuit voltage of the cell. Then the photoelectrical conversion efficiency (PEC) can be determined from formula:

$$PEC = \frac{FF \times Jsc \times Voc}{P_{in}}, \qquad (2)$$

where P_{in} is the density of the illuminating power, in mW/cm^2. From the calculation results, FF and PEC were found to be of 0.54 and 2.6%, respectively.
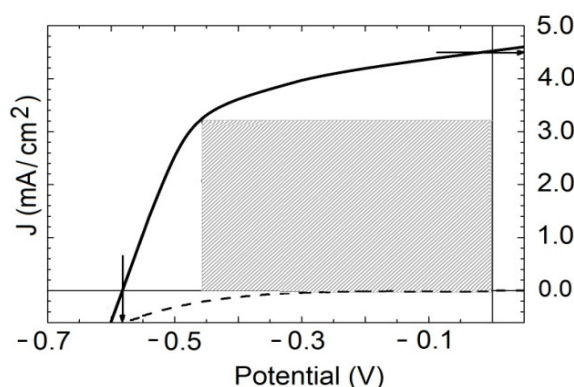

Fig. 6. Current-voltage characteristics of the HOSC measured in dark (dash line) and in illumination light with a power of 56 mW/cm^2 (solid line), showing Voc = 0.60 V, Jsc = 4.60 mA/cm^2, FF = 0.54.

The fact that the FF is considerably large proves that the conjugate polymer of P3HT is a good matrix where nc-TiO$_2$ nanorods are tightly surrounded. This is because during the spinning process in the spin-coating technique, the TiO$_2$ nanorods can adhere by strong electrostatic forces to the polymer and between themselves, and capillary forces can then draw the P3HT solution around the nanorods into cavities without opening up pinholes through the device. The obtained results show that nc-TiO$_2$/Ti layer have played a role of the negative electrode in OSCs like the ITO electrode in the nc-TiO$_2$ based dye-sensitized solar cell (DSSC). For the HOSC, the illuminating light goes inside through the windows of the Al-cathode, such a device is called reverse OSC. The advantages of this solar cell are: (i) to make Ohmic contacts to the metallic Ti much easier than to ITO electrode, and (ii) a larger collection efficiency of the generated electrons due to numerous TiO$_2$ nanorods embedded within P3HT and PCBM polymers. The PEC of 2.6% is a value that can be comparable to the PEC of a thin

nc-TiO$_2$ based dye-sensitized solar cell or the polymer/nanocomposite solar cell that was obtained after an annealing treatment under the electrical field of – 4V [17].

4. Conclusion

Nano hybrid materials containing heterojunctions of P3HT-PCBM/nc-TiO$_2$ were prepared by spincoating P3HT-PCBM on nano-porous TiO$_2$/Ti electrode. The last was made by thermal annealing Ti-wafers at 700°C for 1.5h. Under illumination of the standard light wavelength (λ = 470 nm), the polymer luminescence quenching was observed at the heterojunctions, resulting in the charge separation. Hybrid organic solar cells with a laminar structure of Al/P3HT:PCBM/TiO$_2$/Ti were prepared. With an illumination power of 56 mW/cm^2, the best performance of hybrid solar cells exhibited reasonable parameters, such as Voc = 0.60 V, Jsc = 4.60 mA/cm^2, FF = 0.54 and PEC = 2.6 %.

Acknowledgements

References

[1] J. S. Salafsky, Exciton dissociation, charge transport, and recombination in ultrathin, conjugated polymer, TiO$_2$ nanocrystal intermixed composites, Phys. Rev. B 59 (1999) 10885.

[2] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Hybrid Nanorod, Polymer Solar Cells, Science 295 (2002) 2425.

[3] T. M. Petrella, P. D. Cozzoli, , M. L. Curri, , M. Striccoli, P. Cosma, G. M. Farinola, F. Babudri, F. Naso, A. Agostiano, TiO$_2$ nanocrystals – MEH, PPV composite thin films as photoactive material, Thin Solid Films 451/452 (2004) 64.

[4] V. M. Burlakov, K. Kawata, H. E. Assender, G. A. D. Briggs, A. Ruseckas, I. D. W. Samuel, Discrete hopping model of exciton transport in disordered media, Phys. Rev. 72 (2005) 075206.

[5] P. S. Thomas, J. Kuruvilla, T. Sabu, Mechanical properties of titanium dioxide-filled polystyrene microcomposites, Mater. Lett. 58 (2004) 281.

[6] S. A. Choulis, M.K. Mathai, V.-E. Choong, Influence of metallic nanoparticles on the performance of organic electrophosphorescence devices, Appl. Phys. Lett. (2006) 213503.

[7] S. A. Carter, J. C. Scott, J. Brock, Enhanced luminance in polymer composite light emitting diodes, J. Appl. Phys. 71(9) (1997) 1145.

[8] A. A. Madhavan, G. G. Kumar, S. Kalluri, J. Joseph, S. Nagarajan, S. Nair, K. R. V. Subramanian, A. Balakrishnan, Effect of Embedded Plasmonic Al Nanoparticles on Photocatalysis of Electrospun TiO$_2$ Nanofibers, J. Nanosci. Nanotechnol. Vol. 12, 2012, pp. 7963 – 7967.

[9] B. C. Thompson, J. M. J. Frehet, Polymer–Fullerene Composite Solar Cells, Angew. Chem. Int. Ed. 47 (2008) 58.

[10] S. Ren, L. Y. Chang, S. K. Lim, J. Zhao, M. Smith, N. Zhao, V. Bulovic, M. Bawendi, S. Gradecak, Inorganic–Organic hybrid solar cell: bridging quantum dots to conjugated polymer nanowires, Nano Letters 11 (2011) 3998.

[11] P. M. Allemand , A. Koch , F. Wudl , Y. Rubin , F. Diederich , M. M. Alvarez , S. J. Anz , R. L. Whetten, Two different fullerenes have the same cyclic voltammetry, J. Am. Chem. Soc. 113 (1991) 1050.

[12] N. N. Dinh, D. N. Chung, T. T. Thao, T. T. Chung Thuy, L. H. Chi, T. Vo-Van, Enhancement of performance of Organic Light Emitting Diodes by using Ti- and Mo-Oxide Nano Hybrid Layers, Materials Science and Applications, 4 (2013) 275.

[13] Y. C. Huang, Y. C. Liao, S. S. Li, M. C. Wu, C. W. Chen and W. F. Su, Study of the Effect of Annealing Process on the Performance of P3HT/PCBM Photovoltaic Devices Using Scanning-Probe Microscopy, Solar Energy Materials & Solar Cells 93 (2009) 888.

[14] S. Ulum, N. Holmes, D. Darwis, K. Burke, A. L. D. Kilcoyne, Xiaojing Zhou, W. Belcher; P. Dastoor, Determining the structural motif of P3HT:PCBM nanoparticulate organic photovoltaic devices, Solar Energy Materials & Solar Cells 110 (2013) 43.

[15] S. H. Yang, T. P. Nguyen, P. Le Rendu, C. S. Hsu, Optical and electrical properties of PPV/SiO$_2$ and PPV/TiO$_2$ composite materials, Composites Part A: Appl. Sci.Manufact. 36 (2005) 509.

[16] C.Y. Kuo, W.C. Tang, C. Gau, T.F. Guo, D.Z. Jeng, Ordered bulk heterojunction solar cells with vertically aligned TiO$_2$ nanorods embedded in a conjugated polymer, Appl. Phys. Lett. 93 (2008) 033303.

[17] G. Heliotis, G. Itskos, R. Murray, M. D. Dawson, I. M. Watson, D. D. C. Bradley, Hybrid inorganic/organic semiconductor heterostructures with efficient non, radiative Förster energy transfer, Adv. Mater. 18 (2006) 334.