P3HT:PCBM BLENDS FOR BULK HETEROJUNCTION SOLAR CELLS: INFLUENCE OF SOLVENT AND THERMAL ANNEALING ON EXCITONIC ABSORPTION

Jarmila Müllerová[1], Vojtech Nádaždy[2], Ľubomír Scholtz[1], Libor Ladányi[1]

[1] Institute of Aurel Stodola, Faculty of Electrical Engineering, University of Žilina, ul. kpt. J. Nálepku 1390, 031 01 Liptovský Mikuláš, Slovakia, [2] Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia

E-mail: mullerova@lm.uniza.sk

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1. Introduction

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is one of the most extensively investigated π-conjugated polymer suitable for photovoltaic applications due to suitable absorption spectrum and potential to be manufactured at low cost [1,2]. Thermal annealing is reported to improve P3HT morphology by stacking polymer in coplanar conjugated segments. In bulk heterojunction solar cells, P3HT as a donor is often blended with methanofullerene (PCBM) as an acceptor. P3HT intrinsic optical properties as well as those of blended P3HT are of particular interest [3] because the absorption spectrum can be altered, e.g. by deposition or post-deposition treatment or the ratio of P3HT:PCBM. In P3HT:PCBM blends severe absorption quenching can occur, indicating the destruction of ordering [2]. Therefore P3HT:PCMB UV Vis absorption should be intensively studied [4]. Here we present a study of excitonic absorption in non-annealed and solvent and thermally annealed P3HT:PCBM thin film blends.

2. Experimental

Investigated samples of [P3HT:PCBM] blends were spin-coated on cleaned (ultrasonically in acetone and isopropanol and UV irradiated) ITO substrates. P3HT:PCBM blends were prepared in dichlorobenzene with concentration of 2 wt %. Solvent annealing was performed in Petri dish with 9 cm in diameter for 20 min. Thermal annealing at 110 °C for 4 min or 20 min in argon atmosphere was used for the comparison with non-annealing effect. Two series of blends were under study, namely 1:1 blend and 1.5:1 blend according to the ratio of P3HT to PCBM. Each series consists of five members with different post-deposition treatments:

1. No solvent and thermal annealing (NSA NTA)
2. No solvent annealing, 4 minutes thermal annealing (NSA TA 4 min)
3. 20 minutes solvent annealing, no thermal annealing (SA 20 min NTA)
4. 20 minutes solvent annealing, 4 minutes thermal annealing (SA 20 min TA 4 min)
5. 20 minutes solvent annealing, 15 minutes thermal annealing (SA 20 min TA 15 min)

The thickness of the samples was measured by Dektak profilometer. The thickness of NSA 1:1 blends was measured to be 236 nm, the thickness of SA 1:1 blends of 225 nm. The thickness of NSA 1.5:1 blends was of 274 nm, of SA 1.5:1 blends of 263 nm.

Optical absorbance of non-annealed and annealed samples was measured using Shimadzu UV-Vis-NIR spectrophotometer in the double beam operation with ITO substrate as a reference sample in one light path (Fig.1). To avoid the thickness dependence of absorbance, absorption coefficients were calculated and then the spectra were background subtracted. Absorption coefficients were found to be relatively high (~ 10^4 cm^{-1}).

3. Results and discussion

The wavelength dependent absorbances (Fig. 1) manifest broad asymmetric absorption peaks at ~ 300 – 600 nm. The absorption shoulder at ~ 300 – 350 nm corresponds to PCBM whilst the dominant peak at higher wavelengths belongs to the P3HT absorption. In Fig. 1 two apparent groups of dependences can be seen corresponding to the P3HT:PCBM blend ratio. The broad peak at ~ 500 nm corresponding to the P3HT absorption is obviously more apparent in case of 1.5:1 blend.

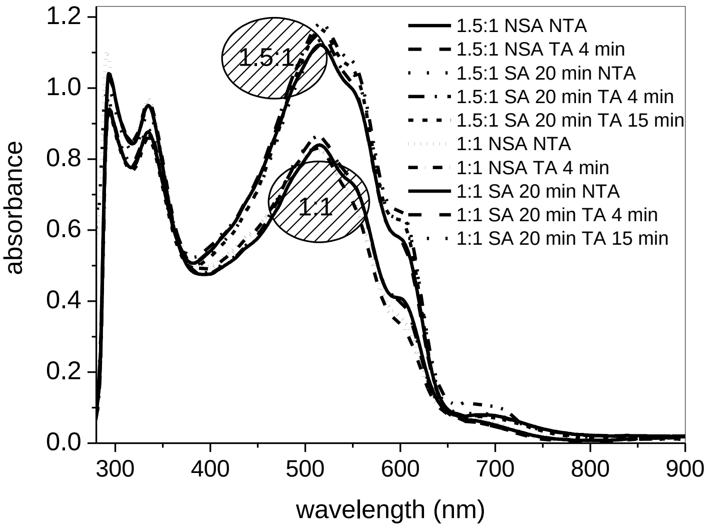

Fig.1: *Absorbance spectra of P3HT:PCBM blends of various post-deposition treatment. The influence of blend concentration is apparent.*

The total P3HT:PCBM blend absorption in UV Vis region can be considered by integrating the area below the peaks. From the integrated absorption, effect of solvent and thermal annealing can be deduced. In both blend series, the integrated absorption after solvent and thermal annealing increases by 5 – 6 % (1:1 blend) and 7 – 10 % (1.5:1 blend) in comparison with not post-deposition processed blends. The highest values of total absorption were achieved in case of SA 20 min, TA 4 min.

Absorption broadening in conjugated polymers arises from the coupling between conjugated segments and from the characteristic distribution of conjugation lengths [5, 6]. The onset of the absorption corresponds to the π–π^* absorption. Excitons (bound electron-hole pairs) are generated when light is absorbed in P3HT. In organic solar cells, exciton generation via absorption is a key process influencing exciton harvesting, i.e. the process of excitons migrating to the donor/acceptor interface and being split into charges.

Therefore, the broad peaks of absorption coefficients were Lorentzian multi-peak fitted. Fig.2 shows an example for 1:1 blend (NSA NTA) for explaining the positions of individual excitations contributing to optical absorption in P3HT:PCBM. The peak at ~ 420 nm (photon energy ~2.95 eV) corresponds to the band-to-band transition and is positioned surprisingly at higher photon energies than in single P3HT films (~2.6 eV) [7]. This shift could be attributed to the influence of PCBM absorption.

Absorption features corresponding to the P3HT excitonic absorption with the participation of Frenkel excitons were found to be at ~ 510 nm (photon energy ~ 2.43 eV) and at ~ 560 nm (~ 2.22 eV) and 610 nm (~ 2.05 eV). The last two are the so-called vibronic sidebands. A Frenkel exciton can be viewed as a delocalized electronic excitation where the electron (occupied LUMO) and hole (unoccupied HOMO) are always positioned in the same molecule. The excitonic absorption at ~ 610 nm indicates a single exciton generation (0-0), at ~560 nm an exciton and one phonon (0-1) generation. The peak at ~510 nm reveals an exciton plus two phonons (0-2) creation (Fig.2).

In all spectra under study excitonic peaks are clearly pronounced demonstrating a certain degree of ordering. In Table 1 some properties deduced from the absorption spectra are presented. We see that the ratio of 0-0 (integrated) absorption to the total absorption in blends increases with post-deposition annealing. We deduce that increased excitonic absorption is due to P3HT chain ordering after solvent thermal annealing enabling more effective exciton harvesting in solar cells. In all blends, the positions of corresponding excitonic peaks in photon energy scale are almost the same and remain unchanged after post-deposition treatments (Table 1). At ~710 nm (~ 1.74 eV) another slight vibronic feature can be observed connected with C=C bond stretching vibrations.

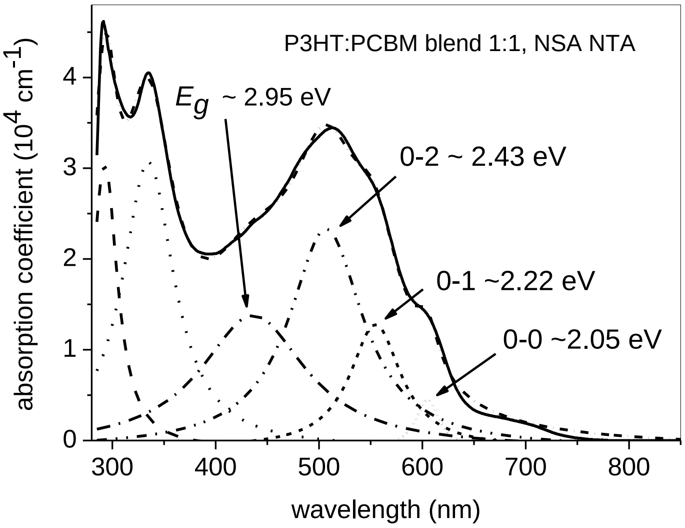

Fig.2: *The decomposition of the absorption spectrum of P3HT:PCBM 1:1 blend (NSA NTA). Individual absorption features are highlighted.*

The vibronic peaks at wavelengths of ~560 nm (~610 nm) corresponding to the 0–0 (0–1) transition result from weakly coupled H-aggregates. The ratio of absorbances in these peaks serves as an indicator of the intermolecular coupling energy. According to the theory of F. C. Spano [8 and references therein] the free exciton bandwidth *W* is inversely proportional to the length of coplanar stacked chain segments, i.e. conjugation length and intrachain order. *W* can be calculated using the ratio of 0-0/ 0-1integrated absorption coefficients $\alpha_{0\text{-}0}$ and $\alpha_{0\text{-}1}$ using the equation

$$\frac{\alpha_{0-0}}{\alpha_{0-1}} \approx \frac{n_{0-1}}{n_{0-0}}\left(\frac{1-0.24W/E_p}{1+0.073W/E_p}\right)^2 \qquad (1)$$

where n_{0-1}/n_{0-0} is the ratio of refractive indices at the 0-1 and 0-0 peak (~0.98 [8]) and E_p ~ 180 meV is the energy of the vibrational mode resulting from the symmetric C=C stretch [8]. Calculated free exciton bandwidths are in Table 1. Relatively high values of *W* indicate in general short conjugation length and low crystallinity of all samples. However, after annealing the free exciton bandwidth decreases which is an indication of the presence of longer conjugation-length segments, i.e. ordering. The free exciton bandwidths were found to be higher for 1:1 blend in comparison with 1.5:1 blend in which higher amount of P3HT assists the chain stacking.

Tab. 1. *Absorptive properties of P3HT:PCBM blends as described in the text.*

Blend	Sample	0-0 /total (%)	0-0 position (eV)	0-1 position (eV)	$\frac{\alpha_{0-0}}{\alpha_{0-1}}$	W (meV)
1:1	NSA NTA	2.4	2.050	2.236	0.39	381
	NSA TA 4 min	2.3	2.054	2.243	0.36	396
	SA 20 min NTA	3.7	2.047	2.228	0.53	311
	SA 20 min TA 4 min	3.4	2.052	2.235	0.49	332
	SA 20 min TA 15 min	3.4	2.053	2.236	0.48	334
1.5:1	NSA NTA	4.4	2.049	2.222	0.54	316
	NSA TA 4 min	4.2	2.052	2.228	0.51	326
	SA 20 min NTA	5.3	2.046	2.219	0.62	283
	SA 20 min TA 4 min	5.1	2.048	2.223	0.59	297
	SA 20 min TA 15 min	5.2	2.050	2.225	0.58	297

4. Conclusions

In this paper excitonic absorption bands of spin-coated P3HT:PCBM blends of two series before and after solvent and thermal annealing have been investigated. The annealed samples showed higher absorption and as we deduced from the free exciton bandwidth calculations – also the ordering. Solvent annealing supports at least the same improvements as known for thermal annealing. The same observation of improved absorption and ordering was found for higher amount of P3HT in 1.5:1 blends than in 1:1 blends.

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