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## THE INFLUENCE OF LiF LAYER AND ZnO NANOPARTICLES ADDINGS ON THE PERFORMANCES OF FLEXIBLE PHOTOVOLTAIC CELLS BASED ON POLYMER BLENDS

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Flexible organic solar cells were successfully prepared using spin-coating technique on PET substrates covered with a thick layer of ITO. The goal of this study is to identify the effects of the LiF layer and ZnO nanoparticles mixing in PEDOT:PSS solution and to compare the photovoltaic properties of these „customized” cells PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/Al, PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al, with ones of the “conventional” structures, PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al. The thickness of the LiF layer, deposited by thermal vacuum evaporation, was two nanometers. Composite samples were prepared by adding ZnO nanoparticles into PEDOT:PSS solution, followed by ultrasonication. I-V characteristics were measured in dark and under A.M.1.5 conditions for all samples immediately and after one month from the preparation date. The action spectra measurements revealed that the structures which have a nanometric LiF layer are more stable than those without. Photoelectrical measurements indicate that the ZnO nanoparticles have a positive influence on the conversion efficiency and also to reduce the serial resistance of the structure.

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**Keywords:** photovoltaic; nanoparticles; spin-coating; ZnO

### 1. Introduction

In the last decade many research groups have focused on the study of organic photovoltaic cells (OPVs) based on polymeric thin films, trying to improve the efficiencies and time stability for these devices. The most common used polymer is poly(3-hexylthiophene-2,5-diyl) (P3HT), as electron donor, in combination with a fullerene derivative, phenyl-C61-butyric-acid-methyl-ester (PCBM), as acceptor, creating a bulk heterojunction solar cell. In this way the new formed structure has the advantage of a maximum contact between donor and acceptor, facilitating the photo-charge carriers' generation and their transport to electrodes. If the electrodes are properly chosen the the interface polymer/electrode form an ohmic contact assuring a good collection of the photogenerated charge carriers [1].

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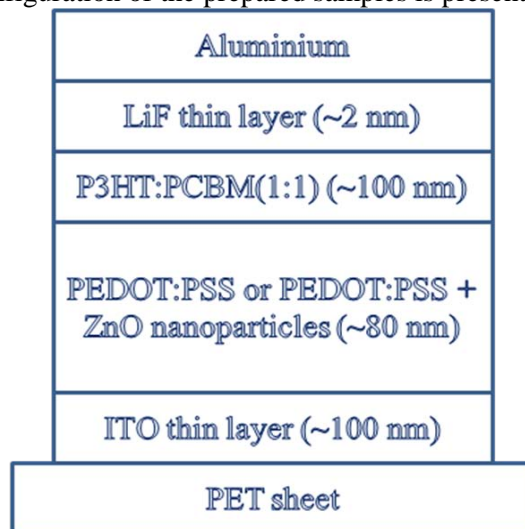
Polymeric thin films have some important advantages as respect to inorganic one, such as: a low cost production, ordinary preparation techniques and adaptability for different substrates like glass or plastic sheets [2], but the morphology of these films strongly influenced the photovoltaic cell performances, which depends on many parameters: one a hand the active layer thickness so the photons absorption to be optimal and on the other hand the materials must have high mobility of charge carriers, so the charge carriers transport to be efficient [3-6].

A major problem for OPVs based on polymeric materials, is related with time stability [2, 7, 8, 9] which is still very poor and the degradation mechanisms are not yet fully understood. The scientists are trying to solve this constraint by changing the morphology [4] or by thermal treatments, or finding a new design of the cells. One of promising solution can be to mix ZnO nanoparticles with P3HT [4, 10, 11] or the insertion of a thin ZnO layer between the anode, which frequently is performed from indium tin oxide (ITO) and the PEDOT:PSS layer [5]. ZnO becomes attractive for these kind of structures because it has good air stability and can be processed by usual techniques at low temperatures [12].

In this paper we analyse, first the influence of ZnO nanoparticles mixed with PEDOT:PSS solution, on the performances of PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/Al and second, the effect of LiF layer deposited below the Al top contact on the performances of PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al photovoltaic cells, comparing with those obtained for conventional PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al structures.. The samples were characterized immediately after preparation and after a month from this date.

## 2. Experimental details

The schematic configuration of the prepared samples is presented in figure 1.



*Fig. 1. Configuration of the prepared photovoltaic cells*

The anode was performed using PET sheets covered with a thin layer of ITO (100 nm), commercially available. The PET sheets were used without further purification. For PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al structures we mixed into 0.5 ml PEDOT:PSS solution 0.1 mg ZnO powder, with the size of nanoparticles smaller than 100 nm. . To obtain a good homogeneity the prepared solution was ultrasonicated for 2 hours and 30 minutes, at room temperature. The PEDOT:PSS + ZnO nanoparticles solution was deposited by spin-coating technique.

The active layer, P3HT:PCBM(1:1) was deposited by spin-coating technique, too, using dichlorobenzene as solvent. A LiF thin layer (2 nm) was deposited by thermal vacuum evaporation. The LiF layer role is to facilitate the electron transfer between the active layer and the back electrode, which in our case was aluminum (Al).

The Al electrode was deposited by thermal vacuum evaporation. The residual pressure in the deposition chamber was  $10^{-5}$  mbar.

The I-V characteristics were recorded in dark and under A.M.1.5. conditions, at room temperature. The measurements were made for as prepared samples and were repeated after one month. The action spectra were performed using a set-up consisting of a Cornerstone 130 monochromator and a Keithley 2400 Source Meter, controlled by a computer. The parameters characterizing the photovoltaic cells, such as: short-circuit current ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF), and power conversion efficiency ( $\eta$ ), were determined for all prepared cells.

### 3. Results and discussion

It is well known that the photovoltaic cells morphology strongly influence the performances of these devices [13]. The most “common” construction for organic photovoltaic’s is Substrate/Anode/PEDOT:PSS layer/Active layer (consisting in a mixture between a polymer and a fullerene)/Cathode. The PEDOT:PSS layer is frequently used because its ability to help smooth the surface roughness and also because its work function lies between the work function of ITO (4.7 eV) and the HOMO levels of the most *p*-type organic semiconductors [14]. The morphology of these devices also influences its stability, which is one of the major problems [13].

The action spectra of PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al structures for as prepared samples and after one month are presented in figures 2a and 2b.

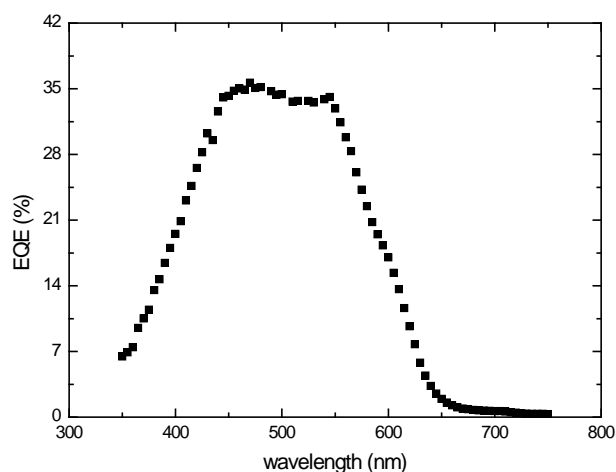


Fig. 2a. Action spectra for PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al as prepared samples

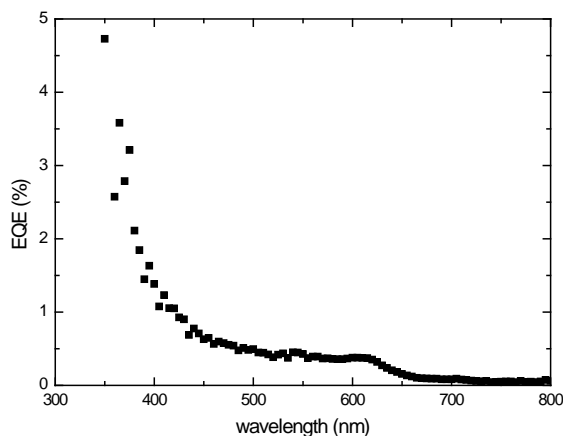


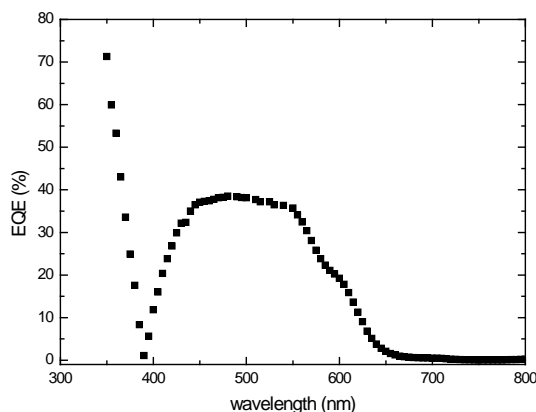
Fig. 2b. Action spectra for PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al

*samples after one month from preparation*

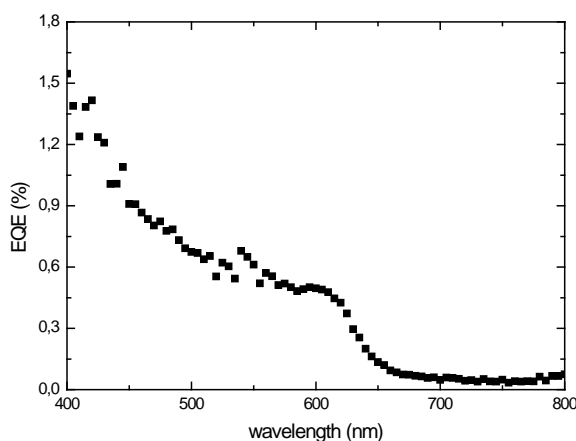
For as prepared samples the EQE value is around 35%, while for the same structures, but after one month from preparation is around 0.45%. As can be observed in the above figures the decrease is very sharp. Taking into account that these samples are "classical", without any additional layer, the assumption of this behavior is related with the diffusion of In from ITO in the active layer, as other scientists already suggest [15,16].

Using the modified form of Shockley equation [9] the values of series and shunt resistances,  $R_s$ ,  $R_{sh}$ , the quality diode factor,  $n$ , and the reverse saturation current,  $I_0$ , were determined, for both as prepared and aged samples. All these data are summarized in table 1.

Trying to improve the stability of these devices we changed the photovoltaic cells morphology by adding ZnO nanoparticles in PEDOT:PSS solution. The obtained samples PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/Al were electrical characterized and the EQE spectra were recorded, at room temperature. In figures 3a and 3b are presented the action spectra for as prepared and aged samples (after one month from preparation date).



*Fig. 3a. Action spectra for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/Al as prepared samples*



*Fig. 3b. Action spectra for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/Al devices after one month from preparation date*

Comparing these data with those obtained for PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al samples we observe that photovoltaic performances were improved, the EQE value for as prepared samples is at most 5% bigger. Moreover, the fill factor, the shunt resistance and the quality diode factor were increased, too. These data will be summarized in table 1.

Time stability for these devices remains a problem (see figure 3b), even though, after one month from preparation date, the EQE still to be small, around 0.6%, it is a little bit higher in the range of maximum sensibility (400-650 nm), than its value obtained for the PET/ITO/PEDOT:PSS/P3HT:PCBM(1:1)/Al (see figure 2b).

If the PEDOT:PSS layer facilitates the holes transport between the polymer blend and the ITO electrode, the LiF layer has the same role, but for electrons. An important parameter in this case is the thickness of LiF layer [14, 17]. By deposition a nanometric layer (0.5 – 2 nm) the photovoltaic performances are increased.

Taking into account that for the samples prepared with ZnO nanoparticles the photovoltaic performances were increased and the samples with LiF are more stable [14], we prepared PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al structures.

The EQE spectrum for as prepared samples and after one month from preparation date are showed in figures 4a and 4b.

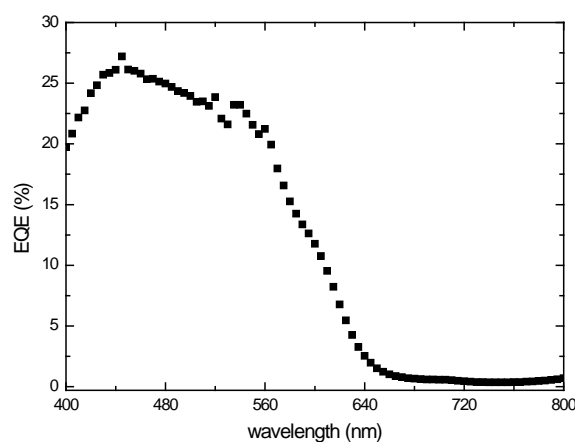


Fig. 4a. Action spectra for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al as prepared samples

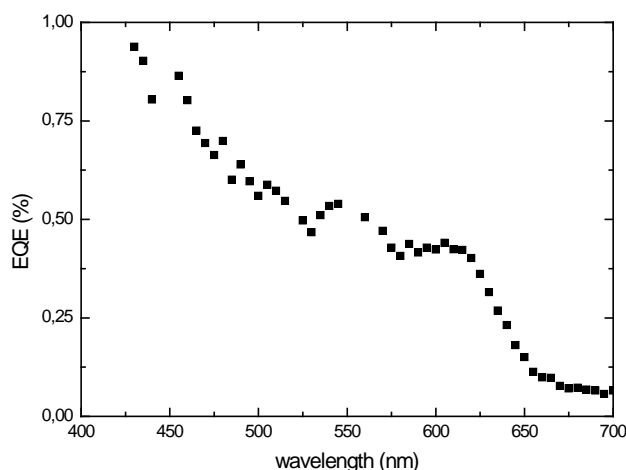


Fig. 4b. Action spectra for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al structures after one month from preparation date

The EQE value for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al as prepared structures was 27%, and after one month from preparation date around 1%. Comparing these data with those obtained for previous described structures we notice that the samples having

a nanometer LiF layer are more stable than those without. Moreover, the values for series and shunt resistances, the quality diode factor and the fill factor were calculated and will be shown in table 1.

Table 1. Parameters characterizing a photovoltaic cells.

Sample	EQE (%)	$R_s$ ( $\Omega$ )	$R_{sh}$ ( $\Omega$ )	n	$I_0$ (A)	FF (%)
PET/ITO/PEDOT/P3HT:PCBM(1:1)/Al As prepared	35	211	$3 \times 10^6$	2.2	$6.7 \times 10^{-10}$	21
After one month from preparation date	0.45	$3 \times 10^5$	$21 \times 10^6$	4	$9.3 \times 10^{-11}$	20
PET/ITO/PEDOT + ZnO np/P3HT:PCBM(1:1)/Al As prepared	40	164	$5 \times 10^4$	2.4	$8 \times 10^{-9}$	22
After one month from preparation date	0.5	$32 \times 10^3$	$3 \times 10^7$	8.2	$5.6 \times 10^{-10}$	28
PET/ITO/PEDOT + ZnO np/P3HT:PCBM(1:1)/LiF/Al As prepared	27	107	$26 \times 10^7$	3.3	$6.3 \times 10^{-8}$	17
After a month from preparation date	0.95	1.54	$28.7 \times 10^7$	6.9	$1.6 \times 10^{-10}$	1.6

The fourth quadrant I-V characteristics in A.M.1.5 conditions for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al photovoltaic cells for as prepared samples and after one month from preparation date are presented in figures 5a and 5b.

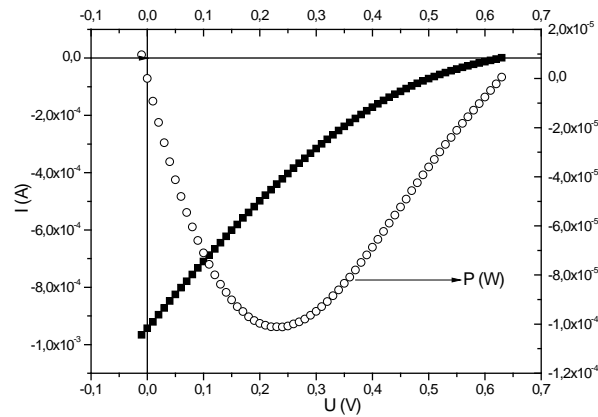


Fig. 5a. The fourth quadrant for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al as prepared samples

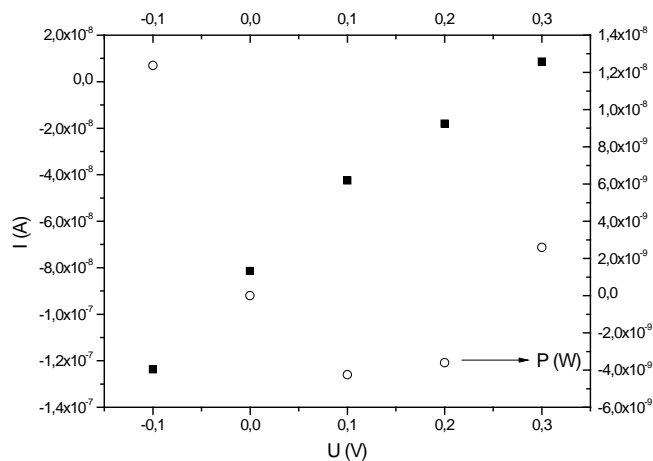


Fig. 5b. The fourth quadrant for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al

*samples after one month from preparation date*

One of the major constraints of these structures is related with time stability (see figures 5a and 5b). If for the as prepared samples the fill factor was 17%, after one month from preparation date the measured value was ten times lower, around 1.6%. Even if P3HT is more stable than other polymers [18], is still an organic material, so is time affected. Exposure to air is one of the factors that strongly influence the sample's life time. The researchers tried to explain this behavior and one of the possible reasons of poor time stability can be related with P3HT radicals oxidation [18]. Another explanation can be the diffusion of PCBM molecules between the P3HT chains leading to a low cristalinity. Further studies are required for improving time stability and for obtaining higher power conversion efficiencies.

## Conclusions

Photovoltaic cells based on P3HT:PCBM(1:1) polymer blends were succesfully prepared by spin-coating technique on flexible substrate. The samples have different morphologies with or without LiF layer and ZnO nanoparticles mixed in PEDOT:PSS solutions. The obtained structures were electrical characterized in dark and under A.M.1.5 conditions immediatelly after preparation and after one month from that date. The samples prepared with ZnO nanoparticles show better photovoltaic performances than those without. The parameters characterizing a photovoltaic cells were determined and we can notice that for PET/ITO/PEDOT:PSS + ZnO nanoparticles/P3HT:PCBM(1:1)/LiF/Al structures were obtained the best results comparing with the other samples analyzed in this paper. A major problem for these devices is related with time stability, after one month from preparation date the external quatum efficiency strongly decrease, almost two magnitude orders for all the prepared samples.

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