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ON THE PHYSICAL PROPERTIES OF INVERTED PHOTOVOLTAIC STRUCTURES BASED ON P3OT:F-SWCNTs ACTIVE LAYER

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We report the fabrication and characterization of glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag inverted organic photovoltaic structures, by spin-coating, in ambient atmosphere. Their electrical and photo-electrical performances were discussed in the frame of morphological properties of constitutive materials of the active layer. The atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) analyzes of pristine and functionalized single wall carbon nanotubes (SWCNTs, F-SWCNTs) showed a significant reduction of formed clusters after functionalization procedure. Moreover, the topography of 97%P3OT:3%F-SWCNTs active layers confirmed the homogeneous distribution of F-SWCNTs within the polymer matrix. The dark current-voltage curves (I-V) proved a good diode behavior, and the parameters characterizing photovoltaic cells (short-circuit current, open-circuit voltage and fill factor) were calculated and discussed.

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1. Introduction

Organic photovoltaic structures (OPVs) attracted interest due to low-cost, lightweight, large covering areas and flexibility facilities [1-5]. Different morphologies, configurations and architectures were studied, but special attention was paid to bulk-heterojunction organic devices based on mixtures between conductive polymers and fullerene derivatives active layers [6-8]. Based on the direction of charge flow two configurations of organic photovoltaic cells, denoted normal and inverted, can be defined. The normal configuration consists of a transparent conductive oxide (TCO) as anode, active layer and a metallic cathode, while for the inverted structures the TCO is behaving as cathode. Reaching power conversion efficiency values exceeding 10% for tandem solar cells [9], the major challenge for organic photovoltaic structures in normal configuration is their poor time stability due to air and moisture exposure. In the case of inverted organic photovoltaic devices the main claim is to find appropriate inter-layers matching their energetic bands with those of donor and acceptor materials. Among many conductive polymers, poly(3-octylthiophene-2,5-dyil) or P3OT is frequently used as donor material due to its early crystalline arrangement and relatively good mechanical and chemical stability [10]. Usually, it is mixed with [6,6]-phenyl C70 butyric acid methyl ester or PCBM, as acceptor material, to compose the active layer of different normal or inverted photovoltaic structures, in planar architecture. Recently, in order to increase the active area and for better harvesting efficiencies, PCBM was replaced with quasi-one dimensional or zero dimensional structures such as single wall carbon nanotubes [11] or zinc oxide nanorods [12].

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In this paper, inverted photovoltaic structures based on P3OT and functionalized single wall carbon nanotubes (F-SWCNTs) were fabricated by spin-coating, in ambient atmosphere. Based on our recent results published elsewhere [13], the added percentage of F-SWCNTs was 3%. The fabricated glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag photovoltaic structures were electrical and photo-electrical characterized, in the frame of the morphological properties of constitutive materials of the active layer.

2. Experimental procedures

2.1. Materials and sample preparation

Single wall carbon nanotubes (78% semiconducting – 22% metallic type; SWCNTs) with 99% purity, diameters in the 1.2 – 1.7 nm range and lengths from 300 nm to 4 μm were purchased from NanoIntegris Inc., and were functionalized using a solution of nitric acid (2.6M HNO_3, 1:1), by refluxing method at 120°C for 18h. Poly (3-octylthiophene-2,5-diyl) (P3OT) and zinc oxide nanoparticles ink (ZnOnp_ink) were acquired from Sigma Aldrich company and were used without further purification. Organic inverted solar cells were fabricated by spin-coating, in ambient conditions, at room temperature, by customizing the active layer as a mixture between P3OT regio-regular polymer and functionalized single wall carbon nanotubes (F-SWCNTs). For all fabricated samples the added percentage of F-SWCNTs was 3%. The preparation procedure consists in subsequent deposition of ZnOnp_ink electron transporter material, P3OT:F-SWCNTs active layer and PEDOT:PSS hole transporter material onto optical glass substrates covered with indium tin oxide (ITO). In order to complete the photovoltaic cell structure, a silver (Ag) thin film, as anode, was deposited, by thermal evaporation (TVE). To remove any solvent traces, as in the case of ZnOnp_ink and PEDOT:PSS buffer layers, or to improve their early crystalline structure, as in the case of P3OT:F-SWCNTs active films, thermal treatments were performed after each deposition. So, after PEDOT:PSS and ZnOnp_ink layers' deposition a thermal treatment at 110°C for 30 minutes was made, while after P3OT:F-SWCNTs active layers the thermal treatment was performed at 70°C for 30 minutes. The annealing was done into oven, in ambient atmosphere. Schematic representation of the architecture of the fabricated photovoltaic cells, together with the band offset diagrams, is presented in figure 1.

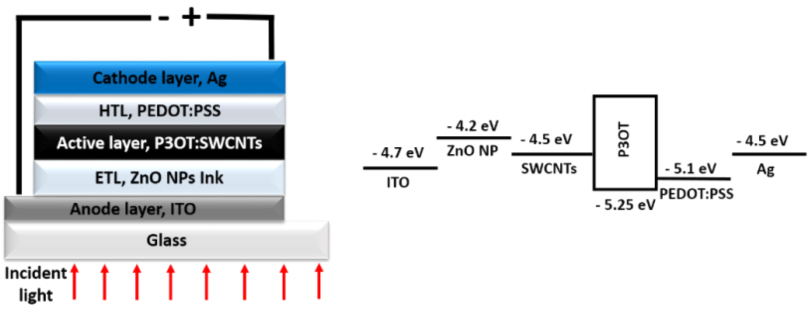

Fig. 1. Schematic representation of the architecture and the band offset diagrams of the fabricated photovoltaic cells.

2.2. Characterization techniques

Spectroscopic analyzes of pristine and functionalized SWCNTs were performed by Raman measurements using visible laser with an excitation wavelength of 532 nm and energy of 2.33 eV. Topography of customized active layers was investigated by atomic force microscopy (AFM), in non-contact mode, while morphological characterization of pristine and functionalized SWCNTs was made by field emission scanning electron microscopy (FESEM). Electrical and photoelectrical measurements of fabricated photovoltaic structures were made in dark and AM 1.5 conditions, in ambient atmosphere, and their performances were discussed.

3. Results and discussions

3.1. Raman spectroscopy results

Full Raman spectra of SWCNTs and F:SWCNTs are presented in figure 2; RBM, D-band and G-band peaks can be easily observed. After functionalization process, due to the nitric acid treatment favoring the attachment of different functional groups to nanotubes' walls, the RBM peak decreased. An opposite behavior was noticed for D-band maximum, indicating the increase of point-like defects in the walls' structure of F:SWCNTs. G-band is associated with in-plane vibrations of sp^2 hybridized carbon atoms, while the value of $\frac{I_D}{I_G}$ ratio informs about the structural quality of carbon nanotubes. In the case of our fabricated samples, the value of $\frac{I_D}{I_G}$ ratio increased after functionalization, proving the increase of the number of structural defects.

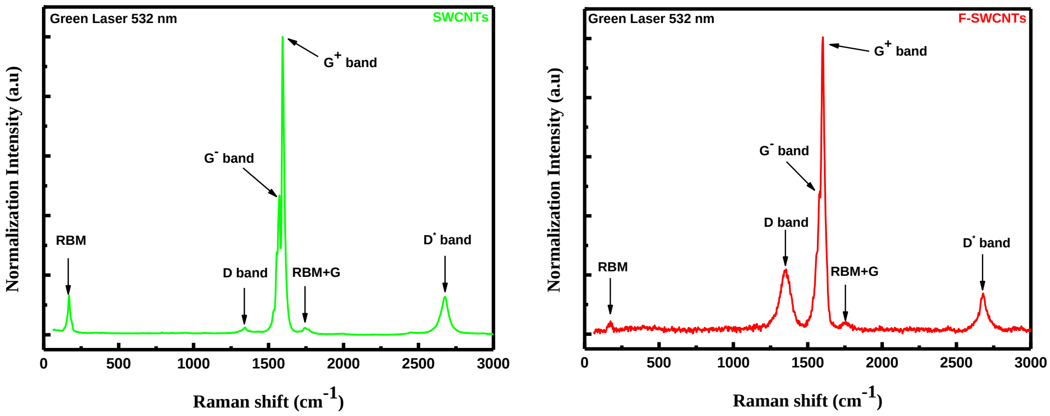

Fig. 2. Raman spectra of pristine (green curve) and functionalized SWCNTs (red curve), recorded using green laser with 532 nm wavelength and 2.33 eV energy.

3.2. Morphological characterization

Field emission scanning electron microscopy (FESEM) images of pristine and functionalized SWCNTs are exposed in figure 3.

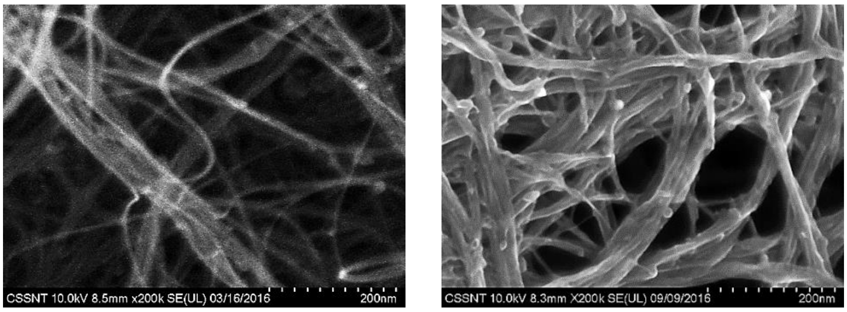

Fig. 3. FESEM images of pristine (left side) and functionalized SWCNTs (right side).

As expected, after functionalization process the density of formed clusters was significantly reduced, altogether with the quantity of residual particles. Moreover, due to the attachment of different functional groups to the walls of nanotubes, the shape of clusters has changed proving functionalization been successfully.

The FESEM images of pure P3OT thin films, together with 97%P3OT:3%F-SWCNTs active layers, deposited onto optical glass substrates, are presented in figure 4.

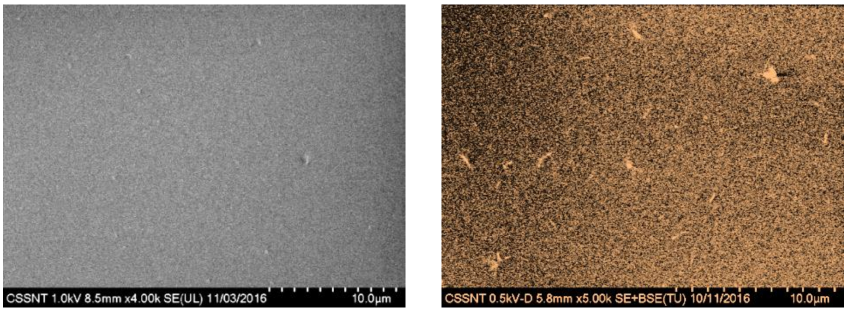

Fig. 4. FESEM images of pure P3OT thin films (left side) and 97%P3OT:3%F-SWCNTs active layers (right side). All analyzed samples were deposited onto optical glass substrates.

Spin-coating deposition technique it is recognized as suitable one to obtain very smooth and uniform surfaces, as in the case of our fabricated thin films. Moreover, the FESEM images of the active layers confirm the homogeneous distribution of F-SWCNTs within the polymer matrix, despite small agglomerations were observed. These results are confirmed by atomic force microscopy (AFM) analyzes, presented in figure 5. Specific parameters like root-mean-square (RMS) were calculated and are depicted in table 1.

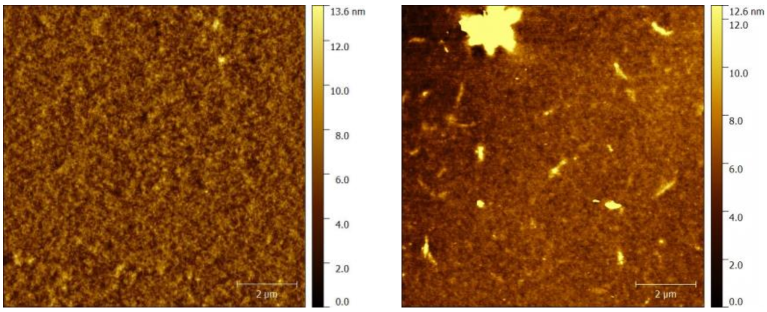

Fig. 5. AFM images of pure P3OT thin films (left side) and 97%P3OT:3%F-SWCNTs active layers (right side). All AFM analyzes were performed in non-contact mode.

Table1. Calculated root-mean-square values of fabricated thin films

Sample	**Thickness (nm)**	**RMS (nm)**
P3OT	105	1.20
97%P3OT:3%F-SWCNTs	110	1.70

3.3. Electrical measurements and photo-electrical behavior

The current – voltage (I-V) characteristics of glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag photovoltaic structures were registered, in ambient conditions, at room temperature. The obtained results are present in figure 6.

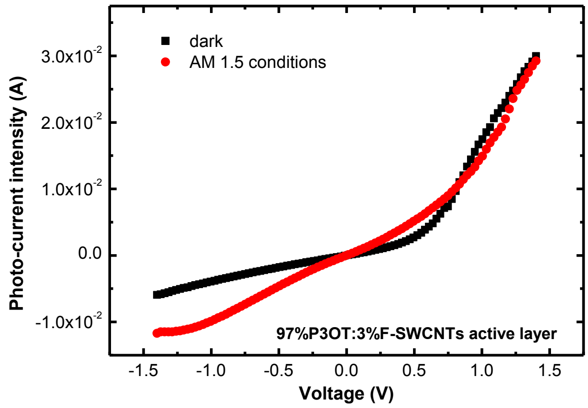

Fig. 6. Electrical and photoelectrical behavior of glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag photovoltaic structures. The obtained results were recorded in dark and AM 1.5 conditions, in both forward and reverse applied bias. For all fabricated samples the active area was 0.4 cm^2.

The obtained current-voltage characteristics in dark of glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag structures proved a good diode behavior, while their photovoltaic performances were poor. The calculated values of short-circuit current (Isc), open circuit voltage (Voc) and fill factor (FF) were determined to be 1.3×10^{-3} mA, 0.02 V and 1.8%, respectively. Based on FESEM, AFM and optical investigations (not shown here) of the 97%P3OT:3%F-SWCNTs active layers we assume that so small values of open circuit voltage are due to the occurrence of two diodes with opposite behavior. Despite that the photocurrent had relatively good values the charge carriers' collection to electrodes was poor leading to a significant reduction of fill factor values. Taking into account that our proposed structures were prepared in a less conventional configuration, further studies are required in order to improve their photovoltaic performances.

4. Conclusions

Inverted organic photovoltaic structures based on poly (3-octylthiophene-2,5-diyl) (P3OT) and functionalized single wall carbon nanotubes (F-SWCNTs) were fabricated and characterized. For all fabricated samples, the added percentage of F-SWCNTs was 3%. Single wall carbon nanotubes (SWCNTs) were functionalized using nitric acid, and the morphological investigation showed a significant reduction of formed clusters after functionalization procedure. The homogeneous distribution of F-SWCNTs within the polymer matrix was confirmed by topography analyzes. The dark current-voltage characteristics (I-V) proved a good behavior, and the specific photovoltaic cells parameters were determined by I-V measurements in AM 1.5 conditions, and discussed. Charge carriers' generation was demonstrated by good values of short-circuit current (Isc), but their collection to electrodes was poor leading to small values of open circuit voltage (Voc) and fill factor (FF). The glass/ITO/ZnOnp_ink/97%P3OT:3%F-SWCNTs/PEDOT:PSS/Ag structures were fabricated in a less conventional geometry denoted inverted configuration, so further studies are required in order to improve their overall photovoltaic performances.

Acknowledgements

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