Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section C: Physical Sciences

CODEN (USA): JCBPAT

Research Article

Fabrication and electrical characterization of solar cells based on poly (o-toluidine), oligothiophene derivatives and nanostructured metal oxide

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Received: 31 March 2018; **Revised:** 17 April 2018; **Accepted:** 25 April 2018

Abstract: A series of solar cells were fabricated using a nanocomposite based on sexithiophène derivatives and nanostructured zinc oxide as blend donor/acceptor active layer. The polymer (POT) and the oligothiophene were synthesized by chemical oxidization. The powders of nanostructured ZnO were prepared by a one-pot solution route at ambient conditions. The solar cells series were fabricated by successive deposition using the spincoating technic, and they are completed by thermal evaporation of Aluminum circular contacts on active layer. The non-linear dark Current-Voltage I(V) characteristics of these devices indicate the presence of a rectifying behavior. The diode parameters were calculated from the dark I(V) characteristics using the modified Shockley equation. On the other hand, the I(V) characteristics measured under illumination indicate a photovoltaic activity. The solar cells parameters are also studied and compared. The short circuit current (Isc) and the open circuit voltage (Voc) of solar cells are improved by incorporation of the POT thin films as hole-transporting layer.

Keywords: Hybrid solar cells, oligothiophene derivatives, nanocomposite, POT interlayer

1. INTRODUCTION

In recent years, intrinsically conducting oligomers and polymers were having considerable attention as a new class of advanced functional materials. Many applications in opto-electronic devices have been developed based on the unique properties of photoactivity, conductivity and other physicochemical properties[1, 2].

Among these oligomers, oligothiophene has many advantages such as a superior solubility and a monodispersity that cannot be easily achieved by conducting polymers[3]. In particular, sexithiophene and its derivatives are intrinsic conducting small molecules that have been extensively studied because of their environmental stability and good processability[4, 5].

Various hybrid solar cells based on organic and inorganic materials as electron donor and acceptor respectively has been investigated[6-8]. In this context, hybrid organic solar cells, based on intrinsically conducting oligthiophene and polythiophene as electron donor and zinc oxide as electron acceptor, have attracted a lot of attention because of their interesting low cost, their flexibility and their moderate power conversion efficiency[6-9].

In the present paper and in continuation of our previous work on organic electronic devices and on solar cells[10, 11], we report on the electronic properties of solar cells based on dialkylated sexithiophene as electron donor and on nanostructured sol gel zinc oxide as electron acceptor. Another structure of solar cells with p-doped poly (o-toluidine) as hole transporting layer (HTL) was studied to understand the influence of the interfacing process. In addition, iodine doping is carried out to investigate the effects of doping on the electronic and photovoltaic properties of solar cells thus fabricated.

2. MATERIAL AND METHODS

The solar cells studied in this work are fabricated in a conventional sandwich structure (ITO/HTL/active layer/Al), they include an indium tin oxide (ITO) coated glass as transparent electrode, a hole transporting layer (HTL), a photo-active layer and aluminum electrode. The ITO coated glass substrates were ultrasound cleaned in acetone and distilled water several times and subsequently air-dried. The photoactive thin films consist of a mixture of conjugated sexithiophene derivatives as electron donor and nanostructured zinc oxide as electron acceptor. Although a doped poly (o-toluidine) was used as an interfacial layer.

2.1. Materials: β,β'-didecyl-sexithiophène (2D6T) has been synthesized by oxidative coupling of the corresponding tertiothiophene derivatives according to the procedure described in reference [12]. Indeed, in a first step we prepare the 3-decylthiophene and secondly, we synthesize the intermediate 3'-decyl-2, 2, 5, 2''-terthiophene. The didecyl-sexithiophène (2D6T) was obtained in a final step by homocoupling of two 3'-decyl-2, 2, 5', 2''-terthiophene using anhydrous copper (II) chloride and butylithium.

The nanostructured zinc oxide (ZnO) has been prepared by a one-pot solution route used in our laboratory[13]. In summary, the hierarchical ZnO nanosheets were prepared by a precursor solution of zinc powder, nitric acid and ethylene glycol. A sodium hydroxide, which acts as precipitating agent, was added drop wise to the previous precursor solution to obtain the desired nanostructured ZnO powders. The obtained ZnO powder consists of several interleaving (agglomerated) ZnO nanosheets [13].

The poly (o-toluidine) (POT) was synthesized from of o-toluidine ($(CH_3)\ C_6H_4NH_2$) monomer by the procedure described in our previous work [11]. Briefly, 5.37 mL of distilled o-toluidine (OT) and 250 mL of (1M) HCl were introduced in an ice bath (T=0◦C). The polymerization reaction is performed under a Nitrogen atmosphere and vigorous stirring by the drop-wise addition of the initiator solution of ammonium persulfate $(NH_4)_2S_2O_8$ (11.41 g) and 250 mL of (1M) HCl. The precipitate is filtered and washed using distilled water and (1M) HCl solution. The obtained polymer is subsequently dried under vacuum. The emeraldine base (EB) form of POT was obtained by deprotonation of the as-prepared emeraldine salt (ES) using (1M) NH_4OH solution.

2.2. Methods: The POT interlayer was deposited by spincoating technic: first, the emeraldine base form of the polymer was dissolved in chloroform at concentration of 1 (wt %). After stirring, the solution is filtered with a 0.45-μm micropore filter to remove any undissolved particles. A few drops of the solution were then deposited on indium–tin–oxide (ITO)-coated glass substrates, which are subsequently spun at a spinning speed of 4000 rpm for 10 s. The thin films based on the emeraldine salt (ES) form (doped POT) were obtained by exposing the EB form of the POT thin films to HCl vapor for 3min.

The active layers based on a blend of sexithiophene (2D6T) and nanostructured ZnO were deposited by the following procedure: A first solution is prepared by dissolving 0,25 g of the 2D6T in 25 mL of chloroform. In another beaker, 0,5 g of ZnO powders was dispersed in 5 mL of methanol: chloroform (20:80) and then stirred. The two lasts solutions are mixed with equal proportions (2D6T: ZnO) and then spincoated on ITO or on ITO/HTL at a speed of 1000 rpm for 1mn.

For iodine doping study, another solution containing I_2 powder (0,3 g) in 100 mL of chloroform are mixed with the last solution based on (2D6T:ZnO), and then spincoated on ITO/HTL at a speed of 1000 rpm for 1mn.

At the end, the device has been finalized by depositing of 1 mm diameter circular aluminum on top of the devices. The aluminum was deposited in a separate vacuum chamber by thermal evaporation of 99,99% purity aluminum shots for three minutes at base pressure of $1{,}5.\ 10^{-5}$ mbar.

The optoelectronic junction properties of our structures were investigated by current-voltage (I-V) in the dark and under illumination using an incandescent lamp (60W).

The electrical measurements were performed on devices at room temperature. The current voltage characteristics were measured using a Keithly 410 programmable picoamperemeter and a 61^0C programmable micro voltmeter. All the instruments are controlled by a computer via a GPIB card.

3. RESULTS AND DISCUSSION

3.1. Current -Voltage characteristics of ITO/2D6T:ZnO/Al device: The Current-Voltage I(V) characteristics I(V) of the sandwich devices, ITO/2D6T:ZnO/Al, measured in the dark and under illumination are shown in **Figure 1**.

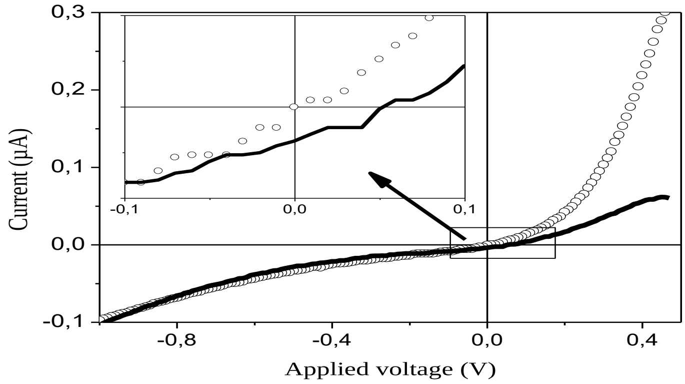

Fig. 1: Current –voltage characteristics of ITO/ (2D6T: ZnO)/Al measured in the dark (circle) and under illumination (line)

In the dark, the I(V) curve is asymmetric and nonlinear suggesting that the (2D6T:ZnO)/Al contact is rectifying. This is in good agreement with other work on Schottky diodes based on sexithiophene [14]. On the other hand, the I-V characteristics measured under illumination shows a photovoltaic activity. Indeed, the ITO/2D6T: ZnO/Al optoelectronic device presents a short-circuit Current of 3, 75 nA, and an open circuit voltage of 50 mV.

3.2. Current -Voltage characteristics of ITO/ doped POT/2D6T: ZnO/Al device: One of the fundamental requirements for efficient operation of hybrid electronic devices is the process of carrier injection / extraction between the electrodes and the active layer. In this context and on the basis of our previous work[10] on organic diodes based on poly (o-toluidine) (POT), the electro-optical properties of this polymer are interesting and are in a major part controlled by the doping process. Therefore, it can be used to promote the transport of charge carriers in optoelectronic devices. In this part, we insert an interfacial layer between the active layer and the ITO transparent conductive electrode. **Figure 2** depicts the I(V) characteristics of ITO/doped POT/2D6T:ZnO/Al photovoltaic devices measured in the dark and under illumination

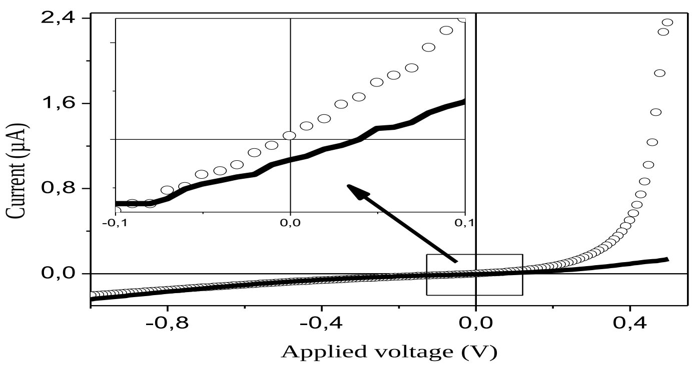

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Fig. 2: Current –voltage characteristics of ITO/ POT/2D6T: ZnO/Al measured in the dark (circle) and under illumination (line)

The cell that contains an interfacial layer based on poly (o-toluidine) doped with HCl shows a short-circuit current of 4,23 nA, and an open circuit voltage of 0,04 mV, suggesting that the POT interlayer make better the photovoltaic response. This result is in good agreement with those reported for organic photovoltaic cells incorporating polyaniline as hole injection layer[15, 16]**.** Therefore, the photovoltaic properties of hybrid solar cells are in a major part controlled by the hole-transporting layer.

3.3. Current -Voltage characteristics of ITO/doped POT/2D6T:ZnO:I_2 /Al device: In the aim of improving the performance of our solar cells, the last part of this work was devoted to the study of the impact of iodine doping on the electronic and photovoltaic properties of the ITO/ doped POT /2D6T:ZnO/Al devices. In **Figure 3** we represents the I (V) characteristics of ITO/POT/2D6T: ZnO: I_2 /Al devices measured in the dark and under illumination**.**

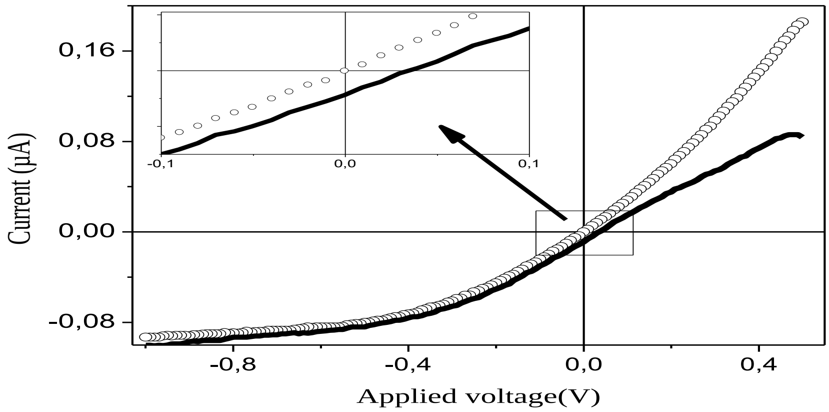

Fig. 3: Current –voltage characteristics of ITO/ POT/DD6T: ZnO : I_2 /Al structures measured in the dark (circle) and under illumination (line)

The last solar cell shows a short-circuit current of 8, 75 nA, and an open circuit voltage of 0, 03 mV, suggesting that the photocurrent have increased from 4, 23 to 8, 75 nA by iodine doping process. This is may be due to the increase in the concentration of the charge carriers (polaron , bipolaron) of the oligthiophene (DD6T). This is in agreement with the research works on the electronic properties of doped organic semiconductors[14-17].

The I(V) measurements of these three structures allows us to conclude that the iodine doping and the POT interlayer have a significant influence on the photovoltaic properties of hybrid solar cells and on the electronic parameters of junctions.

Finally, a theoretical study of the electronic parameters and the conduction mechanisms across the different junctions is necessary to understand these previous results. This study is presented in the next section.

3.4. Theoretical study*:* The I (V) relations of our devices were further analyzed to obtain junction parameters. The current transport across the metal/semiconductor junctions is usually accounted for on the basis of thermoionic emission, Space-Charge Limited Current (SCLC), or Poole-Frenkel emission[18,19]. Indeed, The last two mechanisms are found not to be applicable for our structures in the exploited voltage range. But, the thermoionic emission is found to be applicable in the exploited voltage range, as revealed by fitting his law to experimental data.

In this context, the modified Shockley model taking into account the series and shunt resistances (R_s and R_{sh} respectively) of the structure was used. It is described by the following equation[18]:

$$I = I_0 \left[\exp\left(\frac{q(V - R_s I)}{\eta kT} \right) - 1 \right] + \frac{V - R_s I}{R_{sh}} \qquad (1)$$

Where, I_0 is the saturation current, q is the elementary charge (e), V is the applied voltage, k is the Boltzman constant, η is the diode ideality factor and T is the absolute temperature.

In the **figure 4 a-c**, we represent the experimental I(V) characteristics (circle) of the three structures, and their fits in the forward bias region (line) using the modified Shockley model (Eq.1).

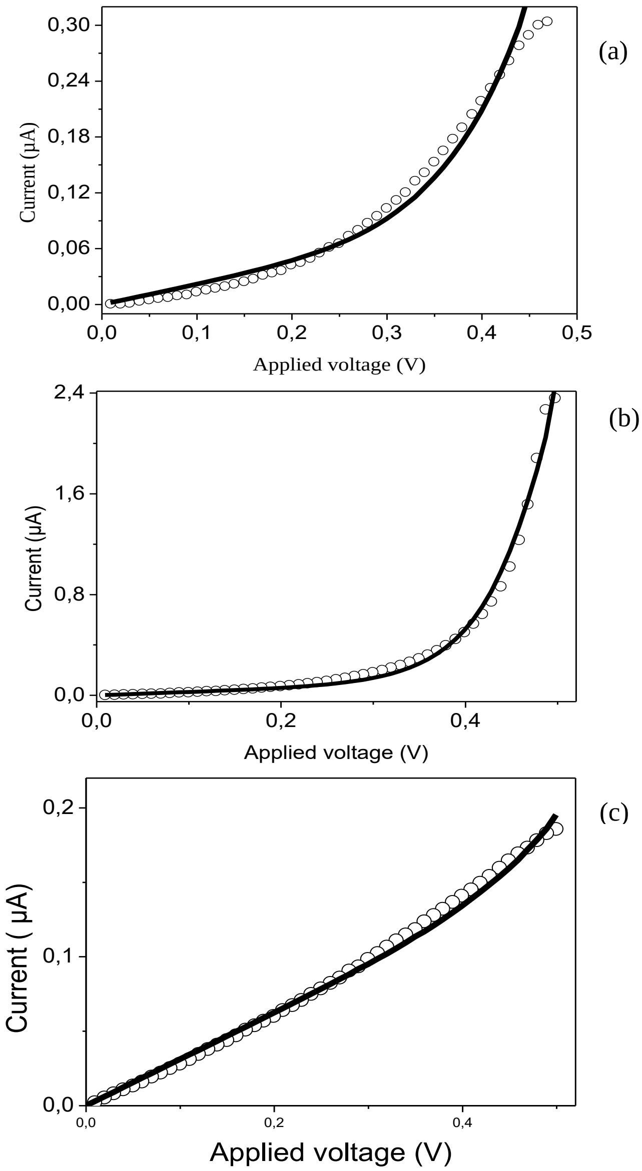

Fig. 4: Experimental I(V) characteristics (circle) and fits (line) using (Eq. 1) of devices: **(a)**: ITO/ 2D6T : ZnO/Al, **(b):** ITO/ POT/2D6T : ZnO/Al, **(c):** ITO/ POT/2D6T : ZnO: I_2 /Al

For the tree fabricated solar cells, it is clear that this model accounts well for the experimental data over the explored voltage range in the forward bias region.

The electronic parameters such as the ideality factor (η), the saturation current (I_0), the series resistance (Rs) and the shunt résistance (Rsh) are calculated from the fits (eq.1) of the experimental dark I(V) characteristics of the device, and summarized in **Table 1.**

Table1: The electronic parameters of the fabricated solar cells

The fabricated solar cells	I_0 (A)	Rsh (kΩ)	Rs (kΩ)	η
ITO/(2D6T : ZnOns)/Al	$1.59\ 10^{-10}$	4600	235	1,99
ITO/ doped POT /(2D6T : ZnOns)/Al	$1.69\ 10^{-10}$	3900	5.9	1,95
ITO/ doped POT /(2D6T : ZnO:I_2)/Al	$1.75\ 10^{-10}$	2600	690	2,5

The deviation of ideality factor of the different structures from the ideal value may be due to the following effects[18,19]:

- Recombination phenomenon in the acceptor/donor interface.
- Presence of barrier in homogeneities as well as the reactive nature of Al contact.
- Possibility of presence of other conduction mechanisms such bulk limited currents in various voltage ranges, trap assisted of tunneling current.

An examination of Table 1 reveals the increasing of the saturation current (I_0) and decreasing of series resistance by using the POT interlayer that promotes the hole injection from the blend active layer to the ITO electrode. Therefore, the change of electronic parameters and the improvement of the photovoltaic response may be due to the effect of POT on the alignment of energy levels between the active layer and the electrode[15,16].On the other hand, the doping process has a significant influence on the intrinsic parameters junctions (η, I_s, Rs and Rsh) and on the photovoltaic parameters (Isc, Voc) of the fabricated devices. These variations can be explained by the change of the carrier mobility in the POT interlayer and/or the recombination phenomenon in the Donor-Acceptor Interface Area (2D6T: ZnO)[16,17].

CONCLUSION

The aim of this work is to produce hybrid solar cells based on oligothiophene as electron donors and nanostructured ZnO as electron acceptors, and also to study the impact of iodine doping and the use of doped POT as hole transporting layer. The poly (o-toluidine), oligothiophene derivatives and nanostructured ZnO were easily synthesized by chemical methods. In addition to that, the thin films were easily deposited by spincoating technic. Therefore, the sandwich devices ITO/2D6T:ZnO/Al, ITO/POT/2D6T:ZnO/Al and ITO/POT/2D6T:ZnO:I_2/Al were fabricated. The most important findings in the experimental study can be summarized as follows:

- It has been observed that the sandwich diodes have asymmetric, non-ohmic rectifying characteristics and the I(V) characteristics of all devices are fitted with the modified Shockley equation to calculate the parameters junction.

- The doped poly (o-tluidine) can be used as holes transporting layer through the ITO electrode in the organic solar cells.
- It has been observed that the iodine doping and interfacing process have a significant influence on altering η, I_0, Rs, Rsh, Voc and Isc parameters.
- The cell that integrates the HCl-doped poly (o-toluidine) as interfacial layer, and (2D6T:ZnO:I2) doped active layer appears the best because it allows having a remarkable short circuit current and open circuit voltage.

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Online publication Date: 25.04.20187