



Experimental investigation of the impact of conducting polymer interlayer and iodine doping on the electronic properties of hybrid solar cells based on alkylated sexithiophene and nanostructured zinc oxide

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Abstract. The influence of poly(o-toluidine) (POT) interlayer as a hole transporting layer (HTL) and iodine doping on electrical properties of hybrid solar cells based on a mixture of didecyl-sexithiophène (2D6T) and nanostructured zinc oxide as blend donor/acceptor-active layer have been investigated. The sexithiophene 2D6T was synthesized by a chemical route through the oxidative coupling of the corresponding terthiophene derivatives, and the nanostructured ZnO powders were prepared by a one-pot solution route at ambient conditions. A series of ITO/(2D6T: nanostructured ZnO)/Al solar cells with and without POT interlayer were fabricated by successive deposition using the spin coating technic, and they are completed by thermal evaporation of aluminium circular contacts on the active layer. The non-linear dark current–voltage $I(V)$ characteristics of these devices indicate a rectifying behaviour. The diode parameters were calculated from $I(V)$ characteristics using the modified Shockley equation and discussed. On the other hand, $I(V)$ characteristics measured under illumination are also presented, studied and compared. The short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of solar cells are improved by the incorporation of the HCl-doped POT thin films and by iodine doping, provided that the iodine concentrations do not exceed 10%.

Keywords. Hybrid solar cells; sexithiophene; nanostructured zinc oxide; poly(o-toluidine); iodine doping.

1. Introduction

In the last few years, intrinsically conducting oligomers and polymers were having significant consideration as a new class of innovative functional materials. Many applications in optoelectronic devices have been established based on the unique properties of photoactivity, conductivity and other physicochemical properties [1,2]. Among these oligomers, oligothiophene has many advantages, for instance, superior solubility and a monodispersity that cannot be easily achieved by conducting polymers [3]. Sexithiophene and its derivatives are inherently conducting small molecules that have been extensively studied owing to their eco-friendly stability and good processability [4,5]. Various hybrid solar cells based on organic and inorganic materials as electron donors and acceptors, respectively, have been investigated [6,7]. In this context, hybrid organic solar cells (OSCs), based on intrinsically conducting oligothiophene

and polythiophene as electron donor and zinc oxide as an electron acceptor, have attracted a lot of attention because of their interesting low cost, their flexibility, and their moderate power conversion efficiency [6,8]. A considerable impact of the dopant and the interlayer kind on the photovoltaic properties of hybrid solar cells has been reported by several authors [9–12]. They reported that the electrical properties are largely controlled by the doping method and by the electron and/or hole transporting layer (HTL), and they concluded that both processes make better the photovoltaic response. Though, to the best of our knowledge, no such study has been conducted on the effects of iodine doping and interfacing by poly(o-toluidine) (POT) on the properties of hybrid solar cells based on oligothiophene and nanostructured ZnO.

In the present study and continuation of our previous work on organic electronic devices and on solar cells [13,14], we report on the electronic properties of solar cells

based on alkylated sexithiophene as electron donor and nanostructured sol–gel zinc oxide as an electron acceptor. And to understand the influence of the interfacing process, we studied another structure with a p-doped POT as a hole transporting layer (HTL). Besides, iodine doping with various amounts of iodine (I_2) is carried out to examine the impact of doping on the electronic and photovoltaic properties of solar cells thus fabricated. Considering these results, the junction parameters and the photovoltaic response of our devices were evaluated using the I – V characteristics measured in the dark and under illumination, analysed and compared. Accordingly, some information on the effects of iodine doping and the interfacing process on the photovoltaic response of our devices are discussed.

2. Experimental

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 a transparent electrode, a HTL, a photoactive layer and aluminium 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 an electron acceptor. Doped POT thin films were 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 [15]. Indeed, in the first step, we make the 3-decylthiophene then, we elaborate the intermediate 3'-decyl-2,2,5',2''-terthiophene using anhydrous copper (II) chloride and butyllithium. The nanostructured zinc oxide has been prepared by a one-pot solution route used in our laboratory [3]. 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 dropwise to the previous precursor solution to obtain the desired nanostructured ZnO powders. The obtained ZnO powder consists of several interleaving (agglomerated) ZnO nanosheets [16]. The chemicals synthesis by oxidation and doping process of the POT, used in the present work as a HTL, have been defined in detail in previous work [13].

2.2 Devices and electrical characterization

The HTL based on POT was deposited by spin coating technic at 4000 rpm for 10 s on ITO-coated glass substrate.

Then the active layers based on a blend of sexithiophene (2D6T) and nanostructured ZnO were deposited by the following procedure; a primary solution is prepared by dissolving 0.25 g of the 2D6T in 25 ml of chloroform. After stirring, the solution was filtered to remove any undissolved particles. In another beaker, 0.5 g of ZnO powders were dispersed in 5 ml of methanol:chloroform (20:80) and then stirred. The two last solutions are mixed with equal proportions (2D6T:ZnO) and then spin-coated on ITO or ITO/HTL at a speed of 1000 rpm for 1 mn. For iodine doping study, another solution containing I_2 powder (0.3g) in 100 ml of chloroform are mixed in various proportions (5%, 10%, 15%) with the last solution based on (2D6T:ZnO), and then spin-coated on ITO/HTL at a speed of 1000 rpm for 1 mn. Finally, the device has been finalized by putting 1 mm diameter circular aluminium on top of the devices. The aluminium was deposited in a separate vacuum chamber by thermal evaporation of 99.99% purity aluminium shots for 3 min at a 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 (60 W). The electrical measurements were performed on devices at room temperature. The current–voltage characteristics were measured via a Keithly 410 programmable picoamperemeter and a 610C programmable microvoltmeter. A computer via a GPIB card controls all the instruments. The schematic illustration of the studied device design is presented in figure 1.

3. Results and discussion

3.1 Current–voltage characteristics of ITO/2D6T:ZnO/Al device

The dark and light $I(V)$ characteristics of the sandwich device, ITO/2D6T:ZnO/Al, are presented in figure 2a. In the dark, the (2D6: ZnO)/Al contact is rectifying, which confirmed by the asymmetric and nonlinear behaviour. This is in good agreement with other work on Schottky diodes based on sexithiophene [3,15]. The $I(V)$ relations of this device were further analysed to obtain junction parameters. Indeed, the current transport across the ITO/2D6T:ZnO/Al junction is usually accounted for based on thermionic emission because this mechanism is found to be applicable

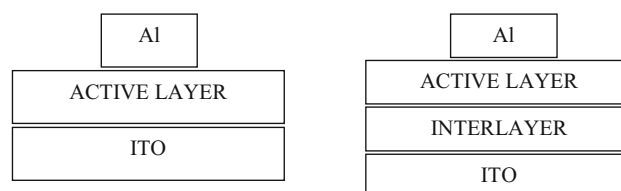


Figure 1. Schematic representation of solar cells configuration without/with interlayer.

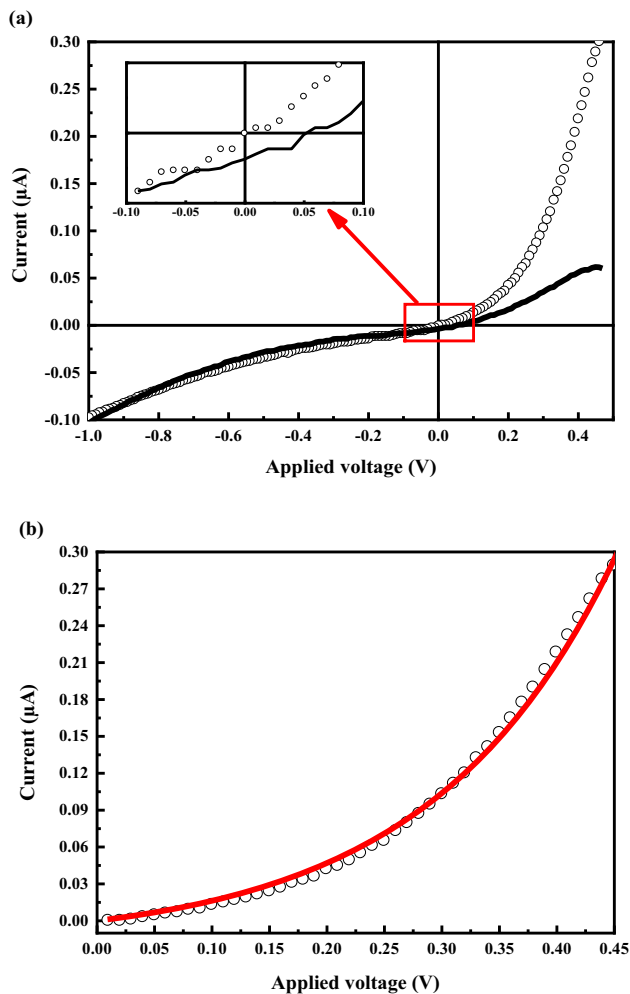


Figure 2. (a) Current–voltage characteristics of ITO/(2D6T:ZnO)/Al measured in the dark (circle) and under illumination (line). (b) Experimental $I(V)$ characteristic of ITO/(2D6T:ZnO)/Al devices measured in the dark (circle) and fits (red line) using equation (1) in the forward bias region.

in the exploited voltage range, as revealed by fitting this law to experimental data [17,18]. In this context, the modified Shockley model considering the series and shunt resistances (R_s and R_{sh} , respectively) of the structure was used. It is described by the next equation [17]:

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

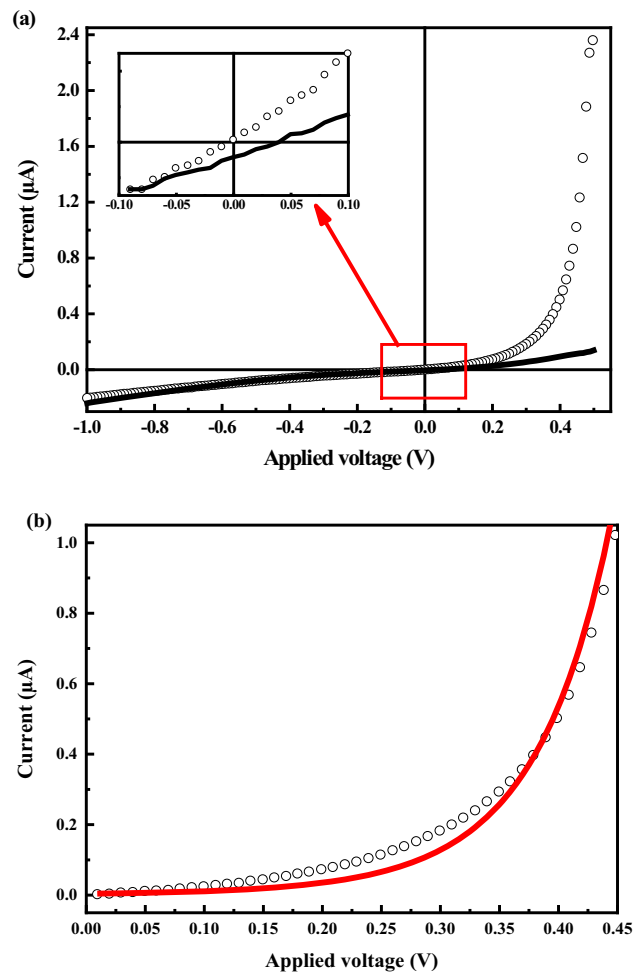


Figure 3. Current–voltage characteristics of ITO/POT/(2D6T:ZnO)/Al measured in the dark (circle) and under illumination (line). (b) Experimental $I(V)$ characteristic of ITO/POT/(2D6T:ZnO)/Al devices measured in the dark (circle) and fits (red line) using equation (1) in the forward bias region.

where, I_0 is the saturation current, q the elementary charge (e), V the applied voltage, k the Boltzmann constant, η the diode ideality factor and T the absolute temperature. As illustrated in figure 1b, this model accounts well for the experimental data over the explored voltage range in the forward bias region. The calculated electronic parameters of the metal/(2D6T:ZnO) junction are given in table 1. Instead, the $I-V$ characteristics measured under illumination shows a

Table 1. The electronic parameters of fabricated solar cells without/with POT interlayer.

| The fabricated solar cells | V_{oc} (V) | I_{sc} (nA) | I_0 (A) | R_{sh} (k Ω) | R_s (k Ω) | η |
|---|---------------------------------|-----------------|-----------------------------------|------------------------|---------------------|-----------------|
| ITO/(2D6T:ZnO)/Al | $0.05 \pm 0.50 \times 10^{-03}$ | 3.75 ± 0.15 | $(1.59 \pm 0.06) \times 10^{-10}$ | 4600.00 ± 378.03 | 235.00 ± 11.75 | 1.99 ± 0.03 |
| ITO/POT _{doped} /(2D6T:ZnO)/Al | $0.04 \pm 0.40 \times 10^{-03}$ | 4.23 ± 0.17 | $(1.69 \pm 0.07) \times 10^{-10}$ | 3900.00 ± 336.00 | 5.90 ± 1.04 | 1.95 ± 0.03 |

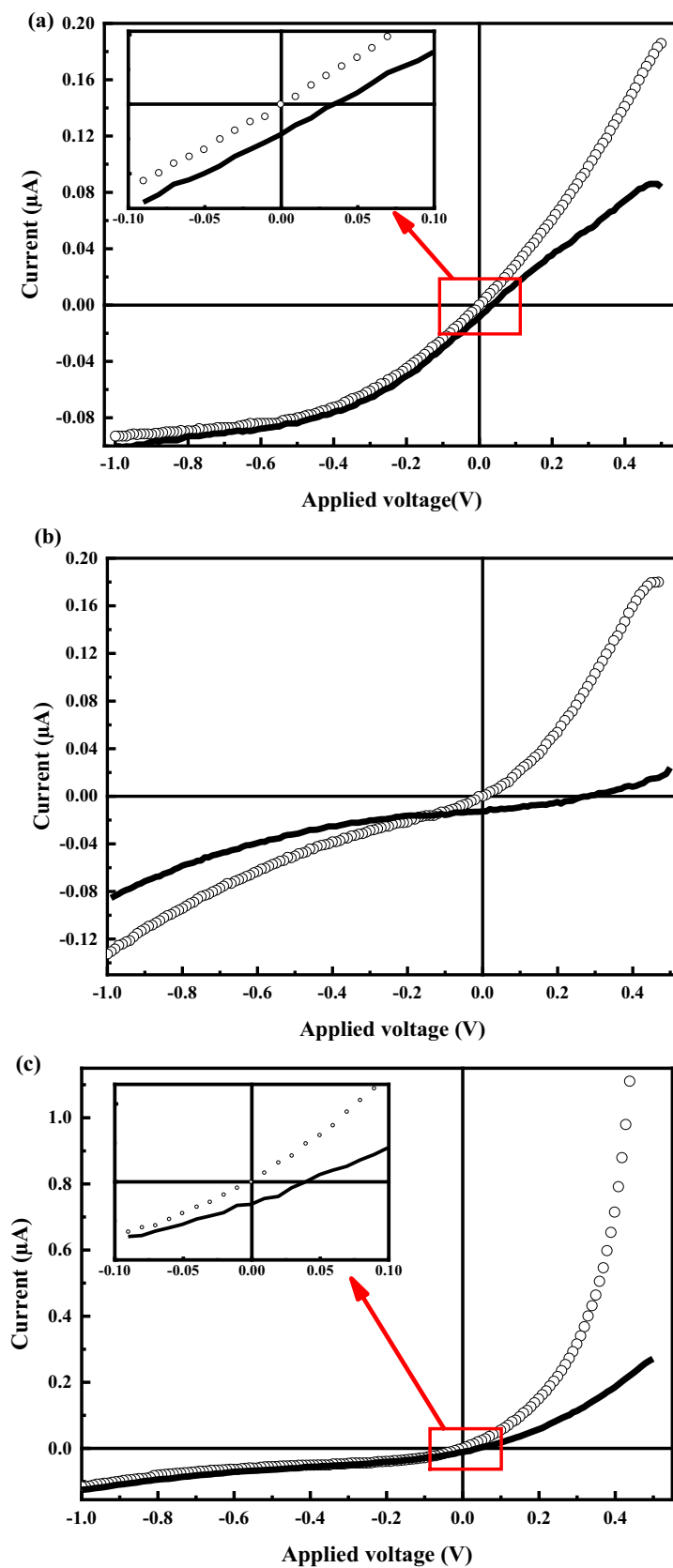


Figure 4. Current–voltage characteristics of ITO/POT-doped/(DD6T:ZnO)_n:I₂/Al measured in the dark (circle) and under illumination (line) with various iodine concentrations of (a) 5%, (b) 10% and (c) 15% of I₂.

Table 2. Electronic parameters of solar cells with different iodine concentrations.

| Fabricated solar cells ITO/POT/(2D6T:ZnO)/Al, with: | V_{oc} (V) | I_{sc} (nA) | I_0 (A) | R_{sh} (k Ω) | R_s (k Ω) | η |
|---|---------------------------------|------------------|-----------------------------------|------------------------|---------------------|-----------------|
| 5% Iodine concentration | $0.03 \pm 0.30 \times 10^{-03}$ | 8.75 ± 0.35 | $(1.75 \pm 0.07) \times 10^{-10}$ | 2600.00 ± 213.67 | 690.00 ± 34.50 | 2.50 ± 0.03 |
| 10% Iodine concentration | $0.27 \pm 2.70 \times 10^{-03}$ | 12.75 ± 0.51 | $(4.70 \pm 0.19) \times 10^{-09}$ | 4620 ± 379.68 | 180.00 ± 9.00 | 4.98 ± 0.03 |
| 15% Iodine concentration | $0.04 \pm 0.40 \times 10^{-03}$ | 11.20 ± 0.45 | $(5.90 \pm 0.24) \times 10^{-09}$ | 2800 ± 230.23 | 31.00 ± 1.56 | 3.10 ± 0.04 |

photovoltaic activity. In fact, the ITO/2D6T:ZnO/Al optoelectronic device presents a short-circuit current of 3.75 nA, and an open-circuit voltage of 50 mV.

The deviation of ideality factor of ITO/2D6T:ZnO/Al Schottky diodes from the ideal value and the weakness of the photovoltaic response may be due to the following effects [11–13,17].

- Recombination phenomenon in the acceptor/donor interface.
- Existence of barrier inhomogeneities as well as the reactive nature of Al contact.

3.2 Impact of a doped POT interlayer

One of the fundamental requirements for the efficient operation of hybrid electronic devices is the process of carrier injection/extraction between the electrodes and the active layer. In this framework and based on our previous work [13,14] on organic diodes based on POT, the electro-optical properties of this polymer are interesting and are in a major part controlled by the doping process. Hence, 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 3a depicts the $I(V)$ characteristics of ITO/doped POT/2D6T:ZnO/Al photovoltaic devices measured in the dark and under illumination. By the same method, the ideality factor (η), the saturation current (I_0), the series resistance (R_s) and the shunt resistance (R_{sh}) are calculated from the fits of the experimental dark $I(V)$ characteristics (figure 3b) of the device and recapitulated in table 1. A careful investigation of table 1 also unveils an improvement of the photovoltaic response of this cell that contains an interfacial layer based on POT doped with HCl. This result is in a good agreement with those described for organic photovoltaic cells incorporating polyaniline as a hole injection layer [19,20]. Also, this improvement can be justified by the increase of the

saturation current (I_0) and by the decreasing of the ideality factor (η) of the junction. The improvement of the photovoltaic response may be due to the raise of the hole injection from the blend active layer to the ITO electrode by increasing the anode work function [17,21]. Therefore, this doped POT can be used as an electron blocking layer and/or holes transporting layer through the ITO electrode.

3.3 Iodine doping of ITO/doped POT/2D6T:ZnO/Al devices

In the aim of enhancing the performance of solar cells, the influence of iodine doping on the photovoltaic and electronic properties of the ITO/doped POT/2D6T:ZnO/Al devices was studied. Indeed, we introduced different proportions of iodine I_2 (5%, 10% and 15%) in the active layer.

In figure 4a, b and c, we represent respectively the $I(V)$ characteristics measured in the dark and under the illumination of ITO/POT/2D6T:ZnO: I_2 /Al devices with various iodine concentrations 5, 10 and 15%. Once again, the characteristic parameters of hybrid solar cells with varied iodine doping concentrations are calculated from the fits of the experimental dark $I(V)$ characteristics (see table 2). Figure 5a, b and c present the experimental $I(V)$ characteristics in the forward bias region measured in the dark for 5, 10 and 15% of iodine doping and their fits using the modified Shockley model (equation 1). It becomes clear that the change of dopant concentrations has a significant influence on the intrinsic parameter junctions (η , I_0 , R_s and R_{sh}) and on the photovoltaic parameters (I_{sc} , V_{oc}) 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) [9,19].

In the case of iodine doping in low proportions (5%), the photocurrent has increased from 4.23 to 8.75 nA. This maybe owing to the increase in the concentration of the charge carriers (polaron, bipolaron) of the oligothiophene (DD6T). This agrees with the research works on the

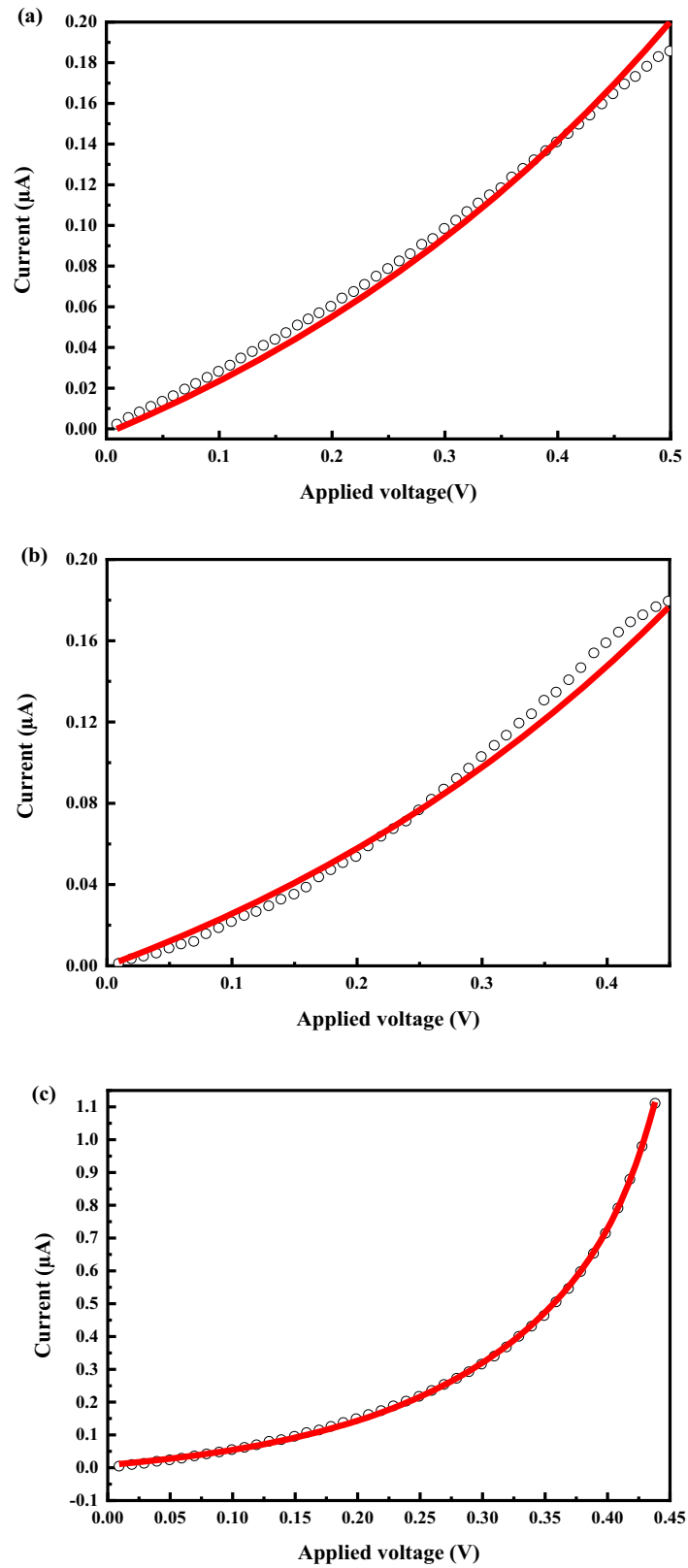


Figure 5. Experimental $I(V)$ characteristic of ITO/POT doped/ (DD6T:ZnO_n:I₂/Al measured in the dark (circle) and fits (red line) using (equation 1) in the forward bias region with various iodine concentrations of (a) 5, (b) 10% and (c) 15% of I₂.

electronic properties of doped small-molecule organic semiconductors [17,22]. The doping by 15% iodine caused the reduction in the photocurrent, this may be due to the decrease in the conductivity in the oligomer (DD6T) and/or in the POT.

Indeed, a high doping rate may increase the effect of the steric hindrance, generated by the iodine ions, on the regularity of the conjugation and the geometry of the 2D6T and/or POT interlayer [4,23]. The cell that integrates the HCl-doped POT as an interfacial layer, and 10% iodine concentrations in (2D6T:ZnO) active layer appears the best, because it allows having a significant increase of short-circuit current values from 4.23 to 12.75 nA and a remarkable increase of the open-circuit voltage from 0.04 to 0.27 V.

4. Conclusions

The main idea of this study is to produce hybrid solar cells based on alkylated sexithiophene as electron donors and nanostructured ZnO as electron acceptors, and to study the impact of iodine doping and the use of doped POT as HTL. The POT-substituted sexithiophene and ZnO nanosheets were easily synthesized by chemical methods. Also, the thin films were easily deposited by spin coating technic. Therefore, the sandwich devices ITO/2D6T:ZnO/Al, ITO/doped-POT/2D6T:ZnO/Al and ITO/doped POT/2D6T:ZnO:I₂ (5, 10 and 15%)/Al were fabricated. We can recapitulate our finding results as follows:

- It has been noticed 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 large value of ideality factor suggests the existence of other transport mechanisms (bulk-limited current and/or trap-assisted tunnelling).
- It has been observed that the change of iodine-doping concentration has significant influence on altering η , I_0 , R_s , R_{sh} , V_{oc} and I_{sc} parameters.
- The cell that integrates the HCl-doped POT as interfacial layer, and 10% iodine concentrations in (2D6T:ZnO) active layer appears the best, because it allows to have a remarkable short-circuit current and open-circuit voltage.

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