Boosting the performance of planar inverted perovskite solar cells employing graphene oxide as HTL

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The numerical simulation tool SCAPS-1D was used to analyze perovskite solar cell having the architecture ITO/ PEDOT:PSS or GO /$CH_3NH_3PbI_{3-x}Cl_x$/ PCBM /Au contains inverted planar hetero-junction device. In this work, we investigated the effect of inserting the Graphene Oxide (GO) as Hole Transport layer (HTL) on the performance of perovskite solar cells. Simulation results show that the use of GO as a hole transport layer is efficient. The efficiency of PSCs based on GO HTL was increased by about 1.6 % compared to the conventional PEDOT:PSS HTL device. The obtained results of optimizing the thickness of GO HTL exhibited an optimum value around 10 nm with an efficiency of 12.35 %, V_{oc} of 1.19 V and FF of 54.8 %. We have also shown that the performance of device for high GO carrier density is a better than with low ones. In addition, increasing the temperature beyond the optimum value obtained around 320 K for both HTL materials (GO and PEDOT:PSS) has detrimental effect on the performance of the perovskite solar cells however the device is more sensitive to the temperature with PEDOT:PSS than the GO ones. The effect of band gap of GO on the performance of device is also studied. The obtained results underline the determining role playedby this parameter with an optimum value around 3.25 eV.

1. Introduction

The upsurge in solar cells efficiency based on thin film perovskite material from 3.8 % to above 26.1 % [1] in the last decade make it possible to consider it as a credible alternative to other thin film materials used in photovoltaic devices such as: amorphous silicon, CIGS, CZTS and CdTe. The perovskite semiconductors have attracted tremendous attention due to their lightweight, low cost, ease of fabrication, solution-based process, and mechanical flexibility [2]. The perovskite solar cells (PSCs) can be designed in two planar hetero-junction configurations: the p-i-n planar configuration, the Hole Transport Layer (HTL) side is used to illuminate the solar cell while in n-i-p planar construction, illumination from the Electron Transport Layer (ETL) side. The perovskite semiconductor, commonly based on organo-lead or organo-tin halide perovskites as light-absorber semiconductors such as $CH_3NH_3PbI_3$, denoted as $MAPbI_3$, and $CH_3NH_3SnI_3$ respectively, is sandwiched between hole and electron conductors which play a critical role in the device mechanism [3]. The role of HTL is not deniable in high performance inverted perovskite solar cells [3] to efficiently extract and transport the photo-generated hole from absorber to the electrode. Various materials, organic and inorganic, have employed as HTL in inverted planar hetero-junction PSCs [4, 5], yet the Poly (3,4-ethylenedioxythiophene): Poly (styrenesulfonate) (PEDOT:PSS) is still, up to now, the most widely used in this devices because of its high work function, high conductivity, high optical transmittance, easy solution process-ability, and potential application on flexible substrates [6-8]. However, PEDOT:PSS also has some disadvantages which reduce the performance of the device, the most important of them the highly acidity which etches

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the ITO, inhomogeneous conductivity and poor mechanical stability in flexible devices in addition to its expensiveness in commercial production [9,10]. Therefore, recent efforts have been devoted to either improve or replace the PEDOT:PSS with other suitable materials.

In addition to the excellent electronic properties, low production cost, large scale production capability and good dispersibility in many solvents, the Graphene Oxide (GO) has several properties and advantages in which it surpass PEDOT:PSS such as: hole mobility which is benefit for high performance solar cells [11,12], band gap energy (3.5 eV), excellent transparency, besides that the GO allows the perovskite film to grow into larger textured domains, resulting in a nearly full coverage, on the contrary of PEDOT:PSS where there are many pores in the film [3]. The research results demonstrate that GO as hole conductor on perovskite thin films in inverted planar hetero-junction PSCs enhances the performance of the device especially the open-circuit voltage (V_{oc}) and the fill factor (FF) [3,13] that make it possible to replace the PEDOT:PSS in perovskite solar cells.

In this work, using SCAPS-1D simulation package [14], the goal is to study the effect of the GO as HTL on the photovoltaic output parameters of $CH_3NH_3PbI_{3-x}Cl_x$ absorber solar cells. We examine the influence of GO layer thickness, the carrier density, band gap energy as well as the effect of the temperature on the performance.

2. Numerical modeling and structure device
2.1. Structure device
Fig.1 shows the structure of modeled solar cell with the energy band diagram. The absorber layer $CH_3NH_3PbI_{3-x}Cl_x$ used in the simulation, in an inverted p-i-n-type planar hetero junction architecture, laid between the p-type semiconductor (PEDOT:PSS or GO) as a Hole Transport Layer (HTL) and n-type PCBM as an Electron Transport Layer (ETL). An Indium Tin Oxide is the transparent conductive oxide with a work function equal to 4.6 eV and metallic Au back contact complete the cell.
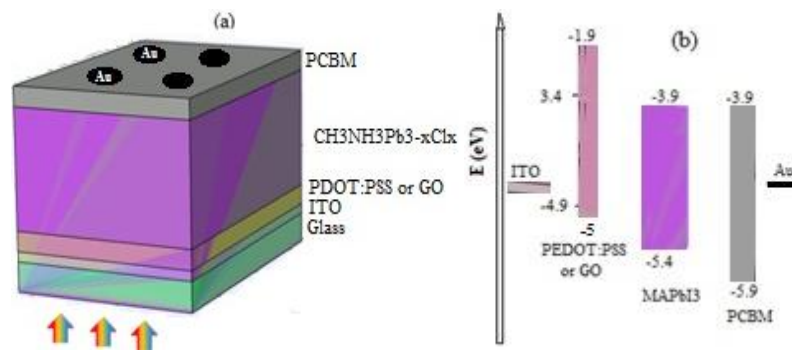

Fig. 1.Schematic representation: (a) layer structure and (b) energy level for the perovskite device.

2.2. Numerical modelling
The software used in this work to model the perovskite-based solar cells is called Solar Cell Capacitance Simulation one dimension (SCAPS-D). This program numerically solves for each point the Poisson equation and the continuity equations for electrons and holes given by:

$$\frac{d}{dx}J_n(x) - e\frac{\partial n(x)}{\partial t} - e\frac{\partial pn}{\partial} = G(x) - R(x) \qquad (1)$$

$$\frac{d}{dx}J_p(x) + e\frac{\partial p(x)}{\partial t} + e\frac{\partial pn}{\partial} = G(x) - R(x) \qquad (2)$$

where J_n and J_p are electron and hole current densities, G(x) and R(x) are the generation and the recombination rates, respectively. This numerical simulation programme, developed by a group of researchers at the University of Gent, Belgium [14], is used to analyses the micro and poly

crystalline and photonic structure, allows the definition of thin-film solar cell devices stacks of layers with a large set of parameters. To describe the recombination currents in deep bulk levels the Shockley-Read-Hall (SRH) model is used. However, an extension of this model describes the defects at the interface [14]. The series and shunt resistances are taken in to account in this study [15]. The defect level of the absorber layer is positioned at the mid band gap and the defect density (N_t) of all layers constituted the cell are fixed at 10^{14} (cm^{-3}). All simulations in this work were performed under illumination standard spectrum AM1.5 with a power density of 100mW/cm^2 and ambient temperature (300 K). The metal electrode in the simulation is chosen to have a work function of 5.6 (eV) (Au) with surface recombination velocity of 10^7(cm/s) and 10^5 (cm/s) for electrons and holes respectively. The values of materials parameters were taken from a numerous published literatures [6-8, 10].

Table 1.Physical and geometric parameters used in the simulation.

	PEDOT :PSS	**$CH_3NH_3PbI_{3-x}Cl_x$**	**PCBM**	**GO**
W (nm)	30	300	60	Var
E_g(eV)	1.6	1.5	2	Var
χ (eV)	3.4	3.8	3.9	1.9
$\varepsilon/\varepsilon_0$	3	6.5	3.9	3
N_c(cm^{-3})	$2.2*10^{22}$	$2.2*10^{17}$	$2.2*10^{19}$	$2.2*10^{21}$
N_v(cm^{-3})	$1.8*10^{22}$	$2.2*10^{19}$	$2.2*10^{19}$	$1.8*10^{21}$
vn (cm/s)	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$
v_p (cm/s)	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$
μ_n (cm^2/Vs)	$4.5*10^{-4}$	2	0.001	100
μ_p (cm^2/Vs)	$9.9*10^{-5}$	2	0.002	300
Doping (cm^{-3})	$1*10^{16}$ (A)	$1*10^{15}$ (I)	$1*10^{16}$ (D)	Var

3. Results and discussions

The current-voltage (J-V) result from simulation using the basic parameters given in Table1 is compared with measurement data from [15] in figure 2. There is a good agreement between the experiment and simulation curves where all parameters: J_{sc}, V_{oc}, FF and conversion efficiency are perfectly similar which validates our set of parameters as a baseline for the simulation in this work.
Compared to PEDOT:PSS solar cell with a similar structure, the device with GO as HTL has a higher open circuit voltage (V_{oc}) Fig.3(a) where we noted an augmentation around 0.3 V. However, the current density (J_{sc}) present slight augmentation (0.1 mA/cm^2) due to the high transparency of both HTL materials, PEDOT:PSS and GO. The photovoltaic parameters derived from Fig.3 (a) are listed in Table 2.The device using the solar cell based on GO shows much higher efficiency compared to that of PEDOT:PSS by about 1.6 % which is completely compatible with the literature [16-18]. Fill Factor decreases by about 10 % due essentially to the V_{oc} which upsurge to 1.193 V. The enhancement of V_{oc} is majorly attributed to the higher Lower Unoccupeted Molecular Orbital (LUMO) energy level of GO which makes it a good electron blocking layer , thereby resulting in the decrease of the charge recombination compared to the PEDOT:PSS. The enhancement of efficiency can be attributed to improved hole mobility, reduced

charge recombination fig.3 (b) and to the work function of GO = 4.9 eV which well matched with that of the absorber (5.2 eV) than the PEDOT:PSS which facilitates the hole transportation to ITO.
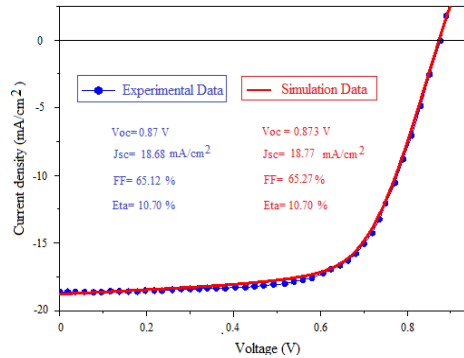

Fig. 2. Comparison between J-V curves of ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/PCBM/Au solar cell for the simulated and the experimental data [15].

Table 2. Comparison of PEDOT:PSS and GO cell performance.

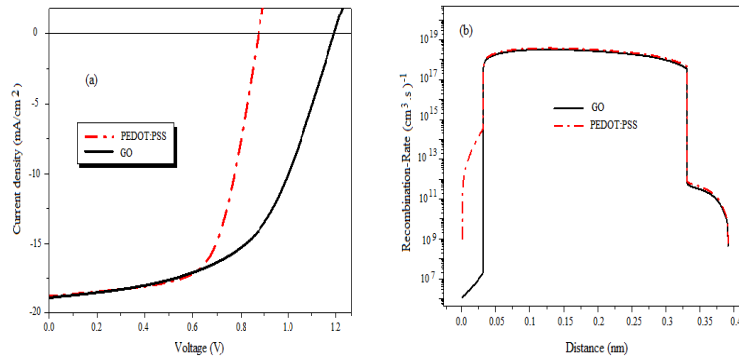| HTL Material	Voc (V)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)
PEDOT:PSS	0.873	18.77	65.27	10.70
GO	1.193	18.87	54.85	12.35

Fig. 3.(a) J-V curves PEDOT:PSS and GO as Hole Transport Layer (HTL), (b) Recombination rate vs position.

3.1. Thickness optimization

To find out the effect of GO thickness as HTL on perovskite solar cells performance, current voltage curves, and electrical parameters represented by Fill Factor and conversion efficiency are reported in Fig. 4(a) and Fig. 4(b), respectively. The thickness of GO HTL is varied from 1 nm to 100 nm. The same trend is observed for the values of FF and efficiency, with a rapid initial increase in those parameters: the FF and efficiency passe from 49.55 % to 54.79 % and from 11.16 % to 12.35 %, respectively, shifting the thickness from 1 to 10 nm. After this value (10 nm) which is consistent with the experimental results [3] the efficiency and FF remain constant even if we further increase the thickness of GO. However, no significant variation versus the thickness of GO for V_{oc} and J_{sc} due to the high transparency of this material.
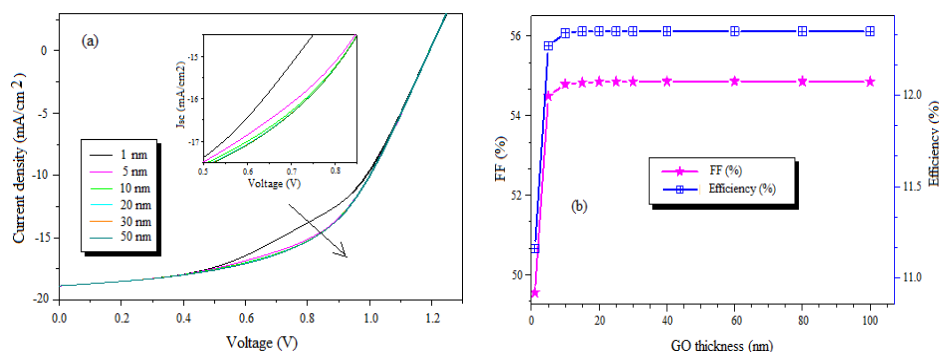
Fig. 4.Predicted for a variety of GO layer thickness (a) J-V characteristics, (b) FF and efficiency for perovskite solar cells.

3.2. Carrier density optimization

This part determines the impact that the hole density of GO HTL has on the perovskite solar cell parameters. The carrier density is varied from 10^{12} (cm^{-3}) to 10^{20} (cm^{-3}) and the thickness of GO is fixed at 10 nm. Since the parameter variations have just minor effect on J_{sc} and V_{oc} only FF and efficiency are shown in Figure 5. As a result, increasing the GO carrier density enhances the FF of the solar cell and thus the power conversion efficiency; we can distinguish two zones of the carrier concentration. The first zone is $N_A < 10^{16}$ (cm^{-3}), where FF and efficiency look a constant behavior because the carrier density is not sufficient to improve the interface to a good ohmic contact. In the second zone corresponds to $N_A > 10^{17}$(cm^{-3}), the parameters are strongly influenced by the augmentation of the carrier density in the GO HTL. The fill factor and the efficiency increase by about 3.5% and 0.8 %, respectively, shifting the hole concentration from 10^{17} to 10^{20} (cm^{-3}).
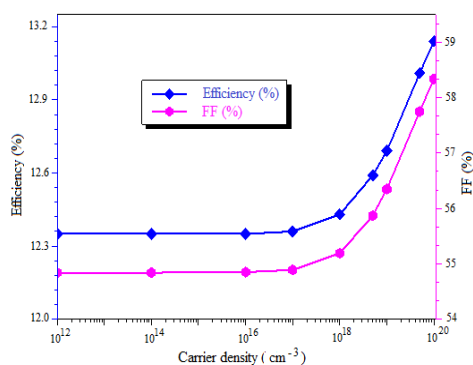

Fig. 5.FF and efficiency as function of GO HTL carrier density.

3.3. Band gap energy optimization

Numerous methods are used to prepare GO such as: Hummer's method, Brodie's method, and Tour's method. The preparation methods affect the amounts of oxygen species in the GO which influence the difference in energy levels between Higher Occupied Molecular Orbital (HOMO) and Lower Unoccupied Molecular Orbital (LUMO) of GO, band gap energy. It is worthwhile to note that the transfer of holes is affected by the energy barrier between the GO HOMO level and the work function of ITO. Figure 6 elucidates the effect of band gap energy of GO, varies between 3-3.6 eV, on the performance of perovskite solar cell. The J_{sc} is very stable towards GO band gap energy variations due to the high transparency of GO. The highest FF and conversion efficiency obtained are 59.36 % and 13.36 %, respectively, which corresponds to an optimum value of band gap around 3.25 eV. The high band gap energy affects the performance of the device more severely than the weak ones, especially for V_{oc}, which drops with the

augmentation of the band gap beyond 3.35 eV. The drop of performance parameters beyond 3.25 eV is potentially a result of the augmentation in energy barrier between GO and ITO.
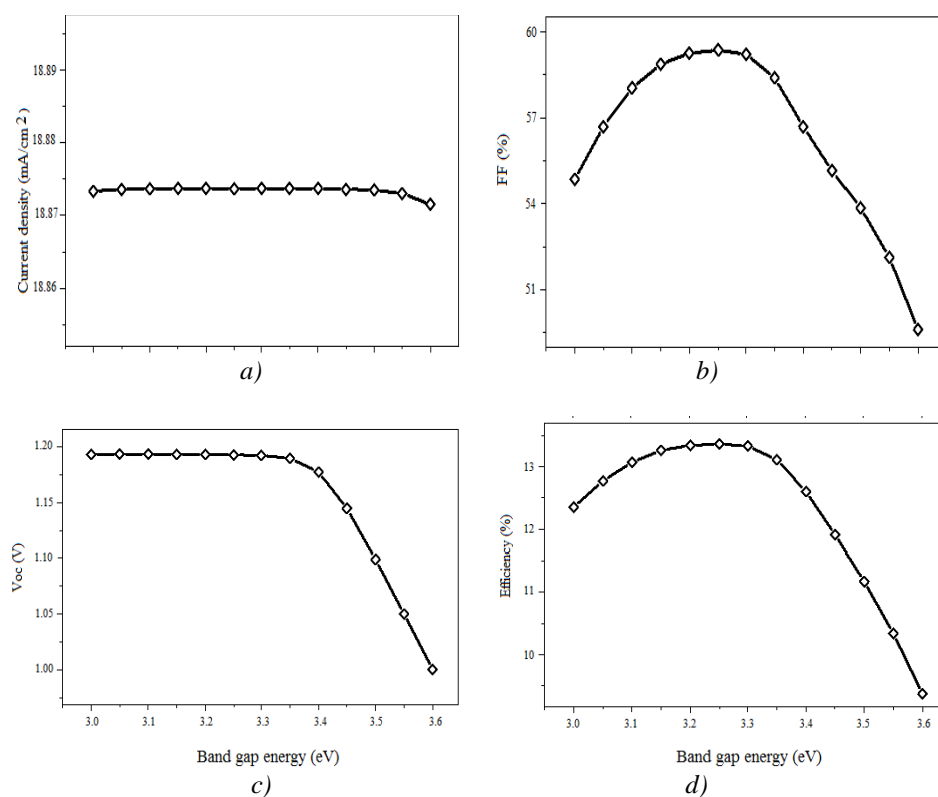

Fig. 6.FF and conversion efficiency vs band gap energy.

3.4. Temperature effect on performance of GO and PEDOT: PSS based perovskite devices

In Fig. 7 we have reported the simulation results of the parameters efficiency, FF, V_{oc} and J_{sc} versus temperature for both materials used as HTL, GO and PEDOT:PSS. Varying the temperature from 200 K to 450 K, we observe that the variation of J_{sc} is insignificant for both materials used as HTL, PEDOT:PSS and GO. Whereas the values of V_{oc} remain constant for lower temperature, around 1.18 V for GO HTL and 0.9 V for PEDOT:PSS. After 300 K the open circuit voltage drops as the temperature rises where we note diminution of 0.3 V and 0.21 V when the temperature varies from 300 K to 450 K for PEDOT:PSS and GO, respectively. Generally, increased the temperature affects positively the fill factor. The conversion efficiency enhances as the temperature rises however beyond 320 K the efficiency drops linearly with slops of 0.019/k and 0.031/K for GO and PEDOT:PSS as HTL, respectively. In conclusion, the effect of high temperature is more crucial on the PEDOT:PSS HTL based perovskite solar cells than the GO ones.
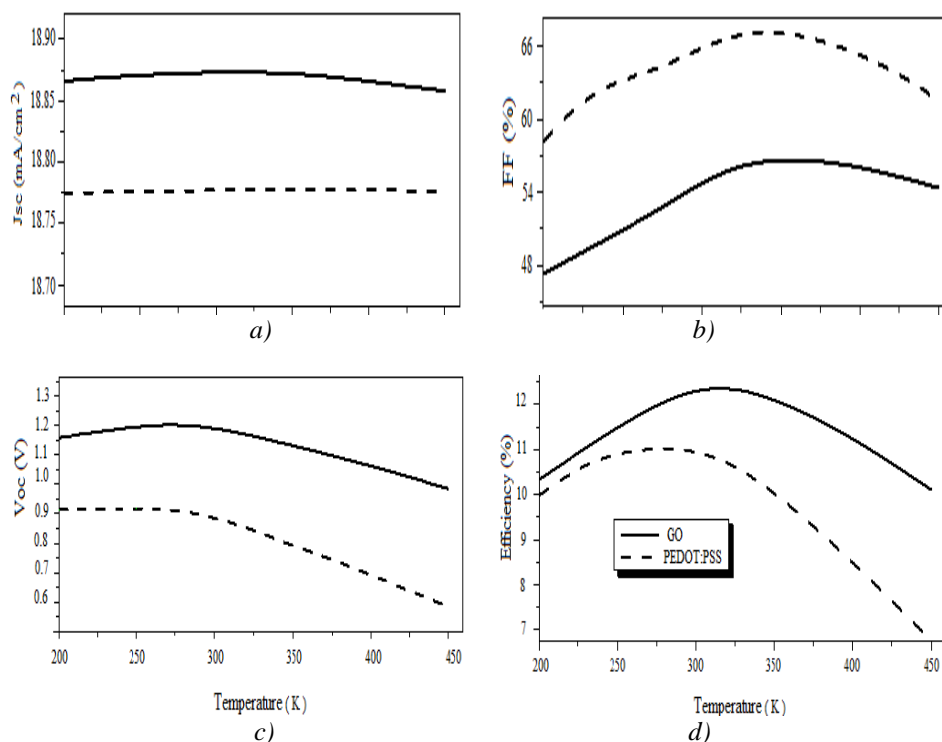
Fig. 7.Various operating temperatures (K) with GO and PEDOT:PSS as HTL layer in perovskite solar cell performance, (a) circuit voltage, (b) circuit current density, (c) fill factor and (d) efficiency.

4. Conclusion

We have presented a simulation work, using the SCAPS-1D software, which allowed us to examine the effect of GO as HTL on the electrical performance of the perovskite solar cell having the architecture ITO/ PEDOT:PSS or GO /CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/ PCBM /Au. The result exhibit an improvement in the conversion efficiency (12.35%) of perovskite solar cells based on GO HTL compared with the reference device (10.7%) based on PEDOT:PSS HTL due to the high LUMO of GO which mitigates the recombination mechanism in this layer. The highest efficiency 12.35 % is achieved when the GO HTL thickness reaches 10 nm after this value the efficiency remains constant even if we further increase the thickness of GO.

The results revealed that the gain in efficiency enhances as the carrier density of GO HTL is increased. The effect of the band gap energy of GO on the performance of the perovskite solar cell structure has also been investigated, the optimum value is around 3.25 eV and the device is more severely affected by the high band gap energy than the weak ones. In addition, the results exhibit that the high operating temperature (> 320K) deteriorates the performance of the device where the efficiency drops linearly with slops of 0.019/K and 0.03/K for GO and PEDOT:PSS as HTL, respectively.

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