

A Planar Heterojunction Perovskite Solar Cell Modified by Graphene Oxide

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Abstract. We developed a perovskite solar cell based on GO/PEDOT:PSS bimolecular layer as hole transfer material. The hole transmission layer can effectively improve the device filling factor and reduce leakage current through effective extraction of holes and effective shielding of electrons. Eventually we increased the device efficiency from 11.4% to 14.1%.

1. Introduction

ABX₃ Perovskite, as a member of calcium titanate structure of materials, has attracted much more attentions due to its excellent photoelectric properties, such as high absorption coefficient, appropriate band gap, long electron diffusion length, bipolar conductivity and high carrier movement [1-3]. Meanwhile, using these unique characteristics, in a few years, the efficiency of perovskite solar cell was significantly increased from 3.9% in 2009 to 23.3% in 2018 [4].

Generally, the perovskite solar cells have two kinds of structures which including meso-superstructured and Planar Heterojunction (PHJ). The previous superstructure is developed from a dye-sensitized solar cell (DSSC) structure, which is composed of porous perovskite films and metal oxides (such as TiO₂ and Al₂O₃) [5, 6]. The highest efficiency is realized by building the superstructure, but the efficiency of true devices usually leads to a huge deviation comparing with the standard device due to the uniformity of superstructure is difficult to be well controlled [7]. The structure of planar heterogeneous introduces the sandwich absorption layer between electron and hole transport layer, solving the problem of the pore filling and simple preparation process which sacrificing the device efficiency [8, 9]. In the plane structure, titanium dioxide is the commonly electron transport material, however, the crystallization process of metal oxide layer usually needs to be in high temperature (500 °C), which is detrimental to prepare the flexible solar cell devices.

To solve this problem, a structure called inversion that can be prepared under low temperature conditions was developed. The typical structure is indium tin oxide (ITO)/ poly (3, 4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT: PSS) / perovskite/fullerene derivatives / Metal electrode [10]. In the multiple layer structure, the interface quality is the key factor to improve the efficiency of the perovskite solar cell. Especially, the electron transport layer and whole transport layer needs to be optimized and processed, so that the photogenic carrier generated in the active layer of perovskite can reach the electrode smoothly. In other word, the carrier recombination and current



leakage at both perovskite-electrode interfaces need to be minimized to achieve high photovoltaic performance. An effective whole transfer material must have the appropriate band level to match the perovskite, good conductivity, high transmittance and good chemical stability [11, 12]. Poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS), due to its high transmittance and the process ability of the solution, makes it the commonly hole transport material used in the planar heterogeneous perovskite solar cell [13-15].

Functionalized graphene and modified graphene oxide materials have been found to be a kind of suitable perovskite solar cell hole transmission material, because it is the electrical conductivity, optical transparency, thermal conductivity, chemical stability and good dispersibility in ordinary solvents, etc [16-21]. The application of GO on polymer solar cells and perovskite solar cells show that the performance is better than that of PEDOT: PSS due to it can effectively extract holes from perovskite and promote the formation of uniform large grains [22-24]. For example, Li et al used the functional modified GO as the buffer layer between the perovskite and HTL to improve the J_{sc} of the device [23], which indicated the band level of GO could prolong the compound of carrier and increased the open circuit voltage V_{oc} and filling factor FF [17]. More importantly, GO's whole mobility is higher than PEDOT: PSS, which is benefit for high performance perovskite solar cells.

In this work, we used GO and PEDOT: PSS as the HTL in perovskite solar cell with the structure of ITO/GO/PEDOT: PSS/ $CH_3NH_3PbI_3$ /perovskite/ [6, 6]-phenyl C61-butyric acid methyl ester (PCBM) / rhodamine 101/Ag. The graphene oxide can carry out good energy band modification to PEDOT in the whole transmission layer of perovskite battery to improve the shielding ability of electrons. Finally, we successfully increased the efficiency of perovskite solar cells from 11.4% to 14.1%. This is mainly due to the effective shielding of electrons from go and the efficient extraction of holes.

2. Experimental section

2.1. Chemicals and reagents

All the used chemicals were purchased from Sigma Aldrich and Alfa Aesar. The precursor of perovskite is to dissolve lead, lead chloride and MAI in the mixture of GBL and DMSO. PCBM is dissolved in chlorobenzene. The precursor solution of perovskite was dissolved completely into solution by stirring.

2.2. Instrumental

The absorption was measured by a U-4100 UV-visible. X-ray diffraction (XRD) measurements were carried out on Phillips X'Pert PRO. A field emission scanning electron microscopy (FE-SEM; SU-8020, Hitachi) was used to investigate the morphology of the perovskite films. The incident photon current efficiency (IPCE) was characterized by using a QEX10 solar cell quantum efficiency measurement system (QEX10, PV measurements, USA). The photocurrent-voltage (J-V) characteristics of the perovskite solar cells were measured with a digital source meter (2450, Keithley Instruments, USA) under AM 1.5G illumination (100 mW cm^{-2}), which was realized using a solar simulator (91192, Oriel, USA, calibrated with a standard crystalline silicon solar cell). J-V curves were measured by scanning from forward bias to short circuit (from -0.2 V to 1.2V) with a scan rate of 0.022 V s^{-1} .

2.3. Fabrication of PSC

The patterned ITO-coated glasses were ultrasonically cleaned in detergent, deionized water, acetone and isopropanol in sequence for 20 min, 30 min, 30 min and 20 min respectively, and then the cleaned ITO-coated glasses were dried under nitrogen flow. Subsequently, the substrates were treated by UV-Ozone treatment for 30 min. The GO with concentration of 1 mg/ml was spin coated onto the ITO-coated glass substrate (4000 rpm, 40 s), followed by baking at 120°C for 15 min. Thereafter, PEDOT: PSS as the hole transport layer (HTL) was spin coated at 8000 rpm for 40s, followed by annealing at 120°C for 20 min. The perovskite films were deposited from a precursor solution containing MAI (1.3

M), PbI_2 (1.26M) and PbCl_2 (0.14 M) in anhydrous GBL:DMSO =7:3 (V: V). The perovskite solution (50 μL) was spin coated with a one-step spin-coating program at 1000 and 3500 rpm for 20s and 40 s, respectively. At 22 s, the wet spinning film was quenched by dropping 160 μl of ethyl acetate. And then is under 100 $^\circ\text{C}$ for 20 min annealing treatment. To cool to room temperature, PCBM is coated on the surface of perovskite film. And then put a layer of rhodamine 101 on it. In the end, the 1.5nm LiF and the Ag electrode of 100nm were thermally deposited under 10^{-6} Torr vacuum.

3. Results and discussion

The architecture of the PSCs with double interlayers is shown in Fig.1a. A thin layer of GO was coated on a pre-cleaned ITO glass. The ITO transparent electrode is used as the bottom anode of the battery. The hybrid bilayer of GO and PEDOT: PSS was chosen as HEL and PCBM as EEL. The perovskite is the absorption layer. Fig.1b represents the energy level of each layer in the device as well as the electron and hole transfer route map. According to the analysis of energy level diagram, PEDOT has good hole transmission capacity, but it is not strong for the shielding ability of the electron. Hau et al adopted PEDOT: PSS as the electronic transmission material [25]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of GO are -4.9eV and -1.9eV. Therefore, holes can be effectively obtained from perovskite through PEDOT and GO to ITO electrode with a minimized potential energy loss. The LUMO of GO (-1.9eV) is much higher than the conduction band (-3.9eV) of the perovskite, and can effectively block the electron. In addition, the LUMO of PCBM is also matched with the conduction band of perovskite, which can promote the transmission of electrons and increase the role of the device filling factor (FF).

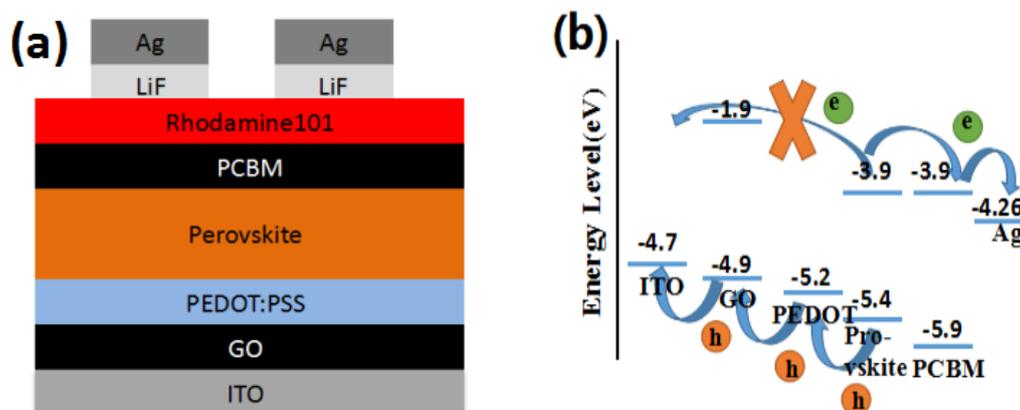


Figure 1. (a) Device architecture and (b) the corresponding energy-band diagram of the devices with GO and PEDOT: PSS hybrid bilayer as the HEL.

For efficient PSC, the maximum reduction of grain size deviation is the most important to control the quality of the perovskite film. Because the surface properties of HTL materials have a great influence on the quality of perovskite films, we have studied the structure and optical properties of perovskite formed on different HTL surfaces. Fig. 2a shows the ultraviolet-visible absorption spectra of perovskite films deposited on different substrates. Here we can understand the influence of GO on the absorption of perovskite films. As can be seen from the figure, both films show a wide spectrum absorption range from visible to near infrared. Moreover, the absorption of the two films indicates that GO will not adversely affect the absorption of perovskite films. Fig.2b compares the steady-state PL profiles of perovskite films deposited under different conditions. We found that the perovskite layer added with GO had stronger PL peak, indicating that the film had higher carrier injection under this condition. However, the position of PL peak was slightly bluish after the introduction of GO, which may be related to the defect caused by perovskite boundary.

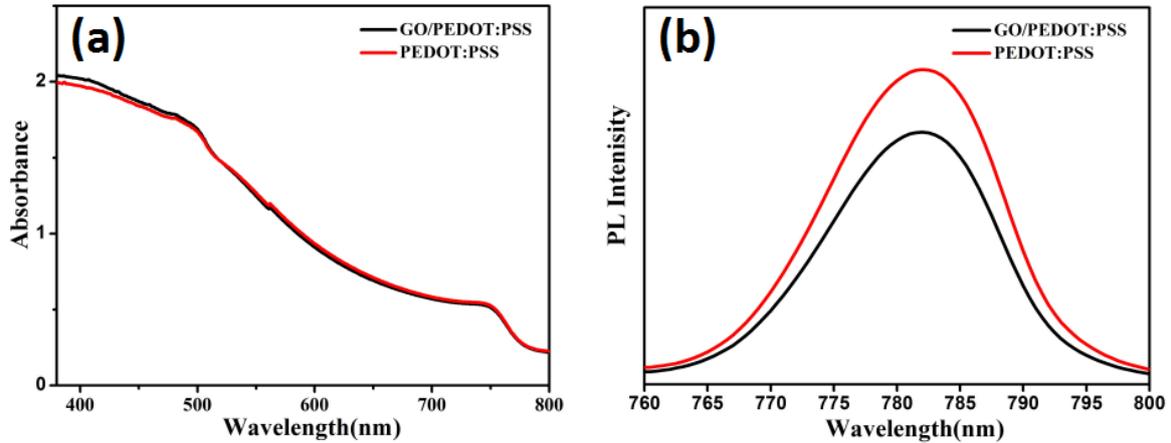


Figure 2. (a)UV-Vis absorption spectra and (b) Steady-state PL spectra of the perovskite films.

In order to further study the effect of HTL on perovskite film, we studied its structural characteristics through XRD spectrum analysis. As shown in Fig.3, in all film XRD spectrum observed a peak of 14.11° , 28° and 31.9° corresponding to the peak of (110), (220) and (310), respectively, which shows that both perovskite membrane has good crystallinity and larger grain size, and in (110) plane with the growth of more priority.

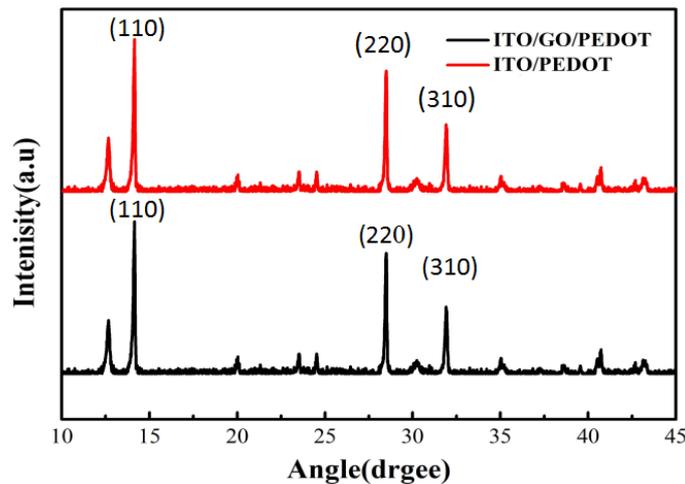


Figure 3. XRD patterns of perovskite films.

In addition, the surface SEM morphology of perovskite films deposited on different HTL was tested under the same conditions as shown as in Fig.4. Two perovskite films were observed to be highly uniform grain size at submicron scale. The perovskite layer is completely covered by PEDOT:PSS layer. The apparent contrast of the structure near the grain boundary is likely to be non-conductive PbI₂, which is consistent with the literature reported by Chen et al [26].

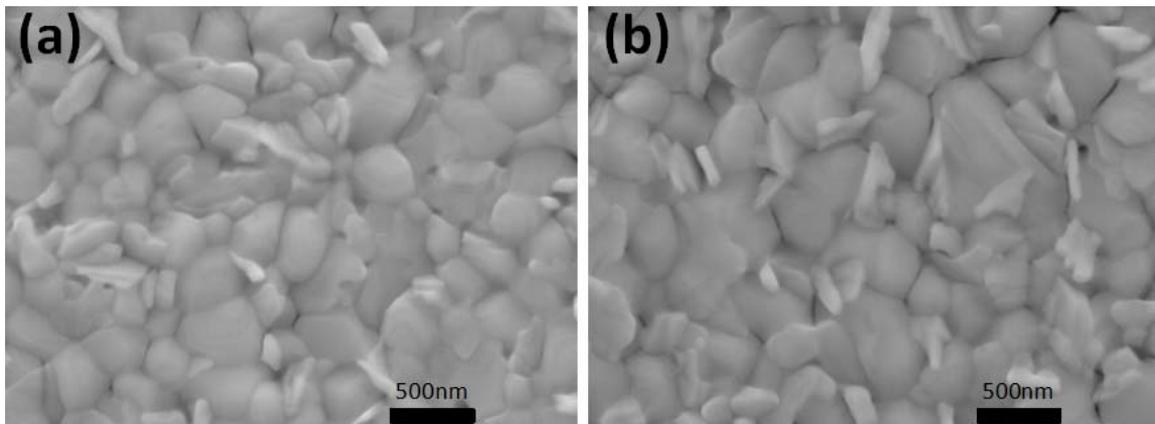


Figure 4. SEM images of perovskite films deposited on (a) ITO/PEDOT: PSS and (b) ITO/GO/PEDOT: PSS.

We further tested the performance of the device. Fig 5a shows the current density and voltage curve (j-v) based on PEDOT: PSS and GO/PEDOT: PSS devices. Table 1 summarizes the photovoltaic parameters of devices at 100 mW cm^{-2} under AM 1.5 G solar illumination. HTL for PEDOT: PSS's device efficiency overall is around 11.4%, its short-circuit current density is 16.5 mA cm^{-2} , and the open circuit voltage V_{oc} is 0.95V and filling factor of 0.73. Since the introduction of GO will increase the serial resistance of the device, which becomes the main factor of the device's efficiency decline. When the three-layer GO is introduced, the optimal efficiency of the solar cell is 14.1%, its short-circuit current is 18.2 mA cm^{-2} , the open circuit voltage is 0.97V, and the filling factor is 0.80. As the number of GO layers increases, the device efficiency decreases, which is caused by the decrease of transmittance and the increase of resistance caused by the increase of thickness. In short, we attribute the improvement of device efficiency to GO's effective transmission of holes and shielding of electrons, which reduces the charge composition and has a significant impact on the open-circuit voltage V_{oc} and the filling factor FF of the battery. In addition, the water solution of PEDOT: PSS is weakly acidic and has a certain corrosion effect on the ITO electrode. After the introduction of GO, a barrier layer can be formed between ITO and PEDOT: PSS to prevent the corrosion of the transparent electrode and improve the conductivity of the electrode.

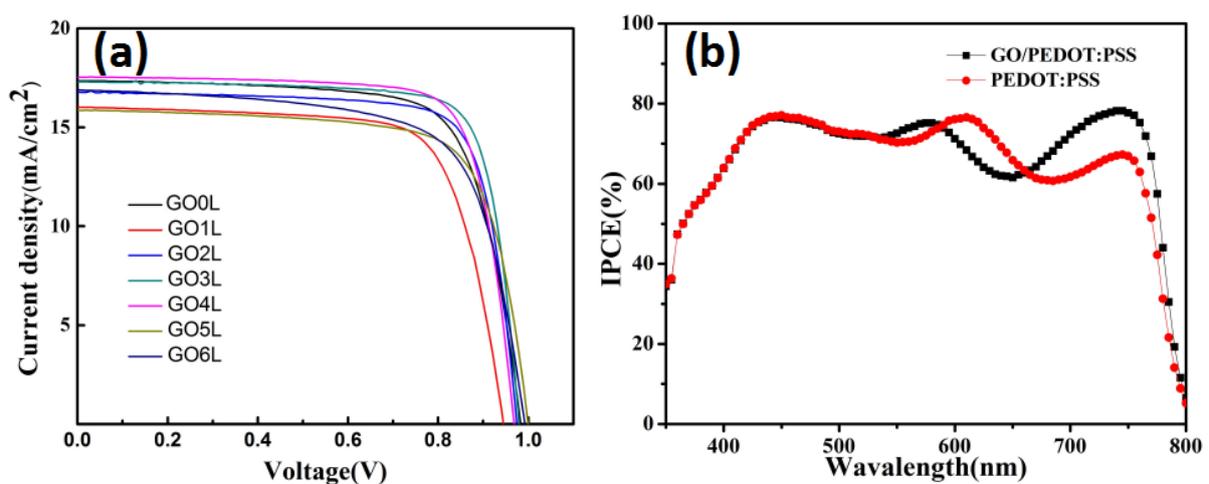


Figure 5. (a) J-V curve of the devices measured under AM1.5G at 100 mW/cm^2 . (b) IPCE spectra of devices ITO/GO/PEDOT:PSS/perovskite/PCBM/rhodamine101/Ag and ITO/PEDOT:PSS/perovskite/PCBM/rhodamine 101/Ag.

Table 1. Photovoltaic parameters of devices.

GO QD layers	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
0	0.95	16.5	73	11.4
1	0.94	16.8	73	11.6
2	0.97	17.6	78	12.9
3	0.97	18.2	80	14.1
4	0.96	18.4	78	13.9
5	0.99	17.8	74	13.0
6	0.99	16.7	69	11.4

4. Conclusion

In a word, we successfully adopted GO/PEDOT: PSS as the hollow transmission material (HTL) of planar heterojunction perovskite solar cell, and the highest photoelectric conversion efficiency of the device was up to 14.1%. Compared with PEDOTPSS as HTL, device efficiency is improved by about 23%. GO can effectively extract holes from perovskite and prevent charge recombination in PEDOT: PSS/ITO layer. Meanwhile, GO also prevents weakly acidic PEDOT: PSS from corroding ITO. All the information indicates that we can use GO/PEDOT: PSS hybrid bilayer as whole transport layer to prepare perovskite solar cell.

Acknowledgments

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