Hysteresis in Hole-free Perovskite Solar Cells with Carbon Counter Electrode Doped Reduced Graphene Oxide (RGO)

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Abstract. Perovskite solar cells achieved high efficiencies but they suffer from the hysteresis of (J-V) curve that depends on the scan direction. The architecture introduced in this paper is hole – free cell with Reduced Graphene Oxide (RGO) as a dopant. The good electrical and optical properties of (RGO) make it acts as a hole transfer layer (HTL) beside its basic role as a dopant of carbon counter electrode. For different areas, the hysteresis decreases by decreasing the cell area. The TiO2/CH3NH3PbI3-xClx interface is truly responsible for the hysteresis in the Perovskite solar cells due to the dependence of the porosity from area to other.

1 Introduction

In recent few years, perovskite solar cells based on $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ have attracted researchers due to their unique properties such as high light absorbance and high power conversion efficiency (PCE) [1]. The first use of $CH_3NH_3PbI_3$ as a sensitizer in solar cells was in 2009 [2], PCE of perovskite solar cells has risen from 3.8% [3,4] to more than 22.3% [5] within eight years. Although the high PCE, anomalous hysteresis appeared in (J-V) curve which made a problem on the cell stability. Hysteresis in perovskite solar cells depends on a lot of factors such as: cell structure, methods of fabrication, measurements methods, capacitive effect [6], and the effect of illumination, temperature and humidity [7]. The reverse scan (from the open circuit to the short circuit current) always shows higher PCE compared to that of forward scan (from short circuit to the open circuit) which introduces the undesirable hysteresis.[8]. The origin of hysteresis has been discussed on the intrinsic properties such as ferroelectric polarization [9], ionic migration [10] ,the charge trapping/detrapping caused by the lattice mismatch or voids at this interface which act as capacitors.

In this paper to discuss the relation between the cell area and the hysteresis we used (RGO) [11] as a dopant of carbon counter electrode to enhance its conductivity, moisture impermeability and photoelectric properties. This leads to favorable physical properties, more charge separation and extraction. Hysteresis is usually small for C-PSCs because the thick TiO_2 scaffold may eliminate charge accumulation at the TiO_2/perovskite interface.[12] .

2 Experimental Works

The perovskite solar cell (PSC) was fabricated by multiple layers; each layer was prepared individually as follows:

2.1 preparation and deposition of blocking layer.

Each pre-cleaned FTO substrate was coated with a 60-nm TiO_2 by spinning a sol-gel solution (0.25 M Titanium Isopropoxide in Ethanol) at 2000 rpm. The layer was dried at 100 °C for 10 minutes and then annealed at 500 °C for 30 min to allow sufficient crystallization in ambient air.

2.2 Preparation and deposition of mesoporous TiO_2 paste.

This layer fabricated as reported in [13] but it was deposited by spin-coating method at 5000 rpm ,the layer was dried at 100 °C for 10 minutes and annealed at 450 °C .The morphology of the mesoporous TiO_2 is shown in Figure.1.

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Fig.1. Morphology of mesoporous titanium dioxide (TiO_2) layer after annealing at 450 °C

2.3 Preparation of Carbon paste doped RGO.

One gram of graphite powder , 0.2 gram of carbon black powder , 0.1 gram of reduced graphene oxide (RGO), and 0.1 gram of zirconium dioxide(ZrO_2) were added into 2 gram α-terpineol under continual stirring for 30 min and then 1.5 gram of ethyl cellulose solution in ethanol (10 wt%) was added into the mixture. The mixture was agitated with a magnetic stir bar for 10 min. Finally, the mixture was stirred vigorously using ball milling for 5 h to get the carbon paste. The normal carbon paste was prepared according to the same procedures as this paste without the addition of RGO. The prepared carbon paste as shown in figure 2 was deposited on the top of the TiO_2 film by the doctor-blading technique, followed by heat-treatment at 500 °C for 30 min.

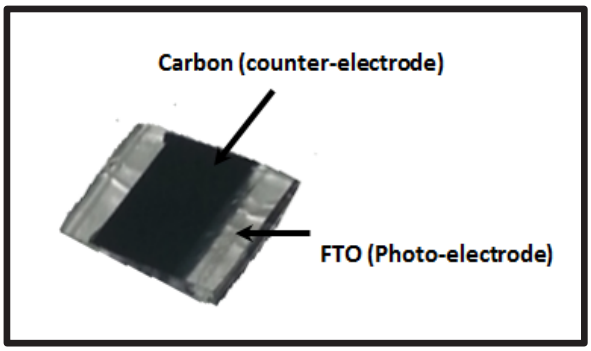

Fig.2. A typical cell with RGO counter electrode layer

2.4 Preparation and Infiltration of Perovskite.

$CH_3NH_3PbI_{3-x}Cl_x$ was synthesized using infiltration method and deposited using spin-coating technique. For the synthesis, 100 µL of precursor solution was prepared by adding 0.5 mL of anhydrous dimethyl formamide (DMF) and 0.5 mL of dimethyl sulfoxide (DMSO) into a mixture of CH_3NH_3I (0.423 g) and $PbCl_2$ (0.246 g). The Perovskite layer has been infiltrated in the mesoprous carbon electrode and then spin-coated as shown in figure 3 inside the glove box at different spin rates (from 1000 - 2000 and 2500 rpm.) for 60 s. Then, the films were annealed on a hot plate for 30 minutes at 100 °C.

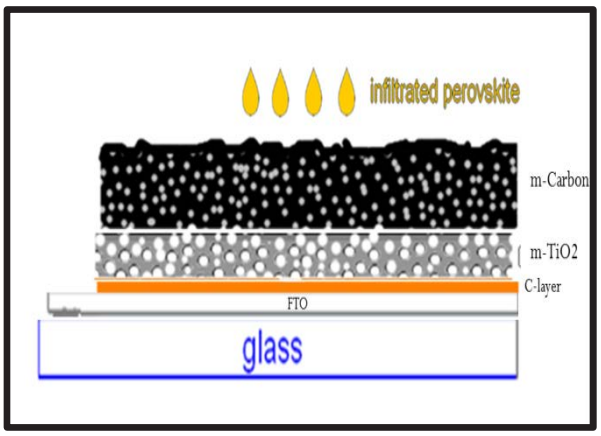

Fig.3. A hole-free perovskite solar cell architecture .

3 Perovskite and Cell characterizations

After the cell fabrication, the cell characterized by exposing a solar cell to a standard light source(xenon lamp) (typically air mass (1.5 AM), and power of 100 $mWcm^{-2}$) and sweeping by applying predetermined biasing voltage range across the terminals of the cell and the current is measured by [kiethely 2635A]. Different parameters ,namely, open circuit voltage (V_{oc}) , short circuit current density(J_{sc}) ,fill factor(FF), power conversion efficiency (PCE) and hysteresis index(HI) are listed in table 1 for different cell areas and different scanning directions(forward-reverse) .The hysteresis index is calculated by[14]:

$$HI = \frac{J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})}{J_{RS}(0.8V_{oc})} \qquad (1)$$

Where: J_{RS} is the current density in reverse direction, J_{FS} is the current density in forward direction.

To examine the surface morphology of the perovskite alone we have used scanning electron microscope (JSM-6360).The structure and phases of the materials are examined byX-ray Diffraction (schimadzu-7000)[11].the absorption and estimated band gap of the perovskite ($Ch_3NH_3PbI_{3-x}Cl_x$) was measured using UV-Visible spectroscopy (EVO300 PC) as shown in next figures(4-6), the absorption peak at the wavelength of around 750 nm of $CH3NH3PbI_{3-x}Cl_x$ film was observed as shown in figure (6) . Perovskite film exhibits very strong absorption intensity [15].

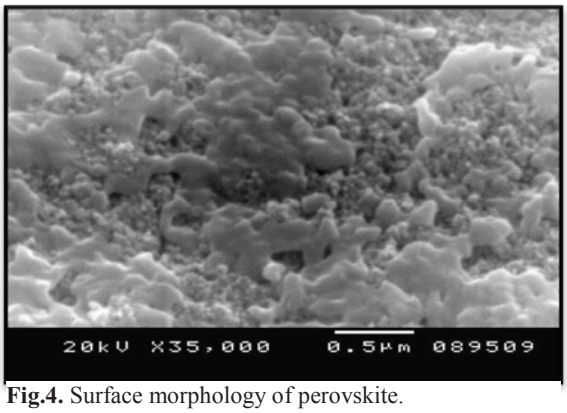

Fig.4. Surface morphology of perovskite.

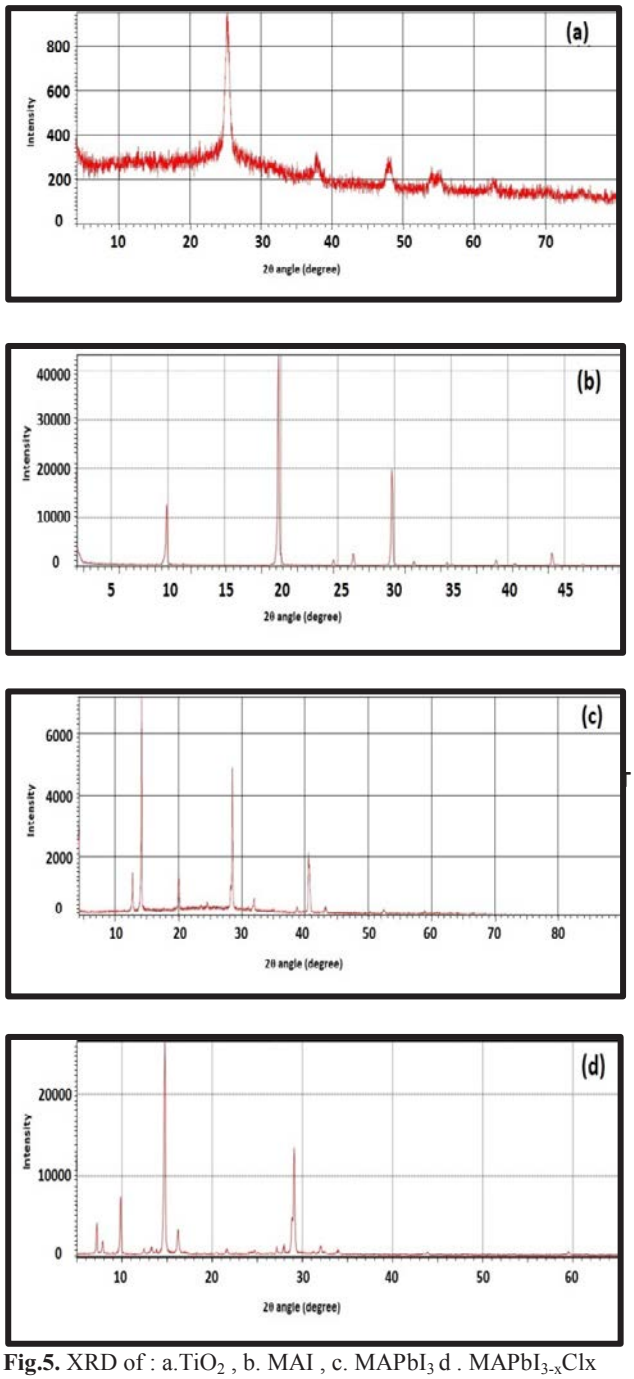

Fig.5. XRD of : a.TiO_2 , b. MAI , c. $MAPbI_3$ d . $MAPbI_{3-x}Clx$

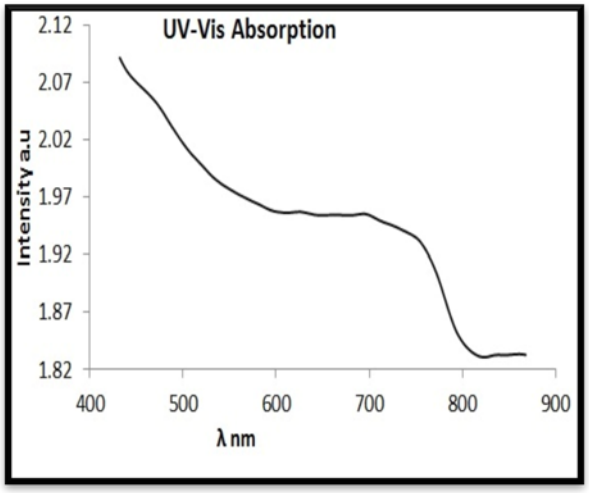

Fig.6. UV–Visible absorption spectrum of $Ch_3NH_3PbI_{3-x}Cl_x$

4 Results

After measuring the (J-V) curve, the results shown in table 1:

Cell area (cm^2)	Scan direction	$\frac{\Delta Voc}{Voc}$%	$\frac{\Delta Jsc}{Jsc}$%	$\frac{\Delta FF}{FF}$%	η%	HI
0.16	REVERSE	+16.5	-65.5	+25.2	0.96	0.13
	FORWARD	+34.4	-66.4	+4.81	0.55	
0.18	REVERSE	+31.6	-55	+24.6	0.67	0.14
	FORWARD	+5.2	-57	+7.5	0.54	
0.20	REVERSE	0	-50	+28.8	0.76	0.22
	FORWARD	+17.5	-34	+19.5	0.28	

Table 1 Reduction in photovoltaic parameters due to Hysteresis.

From the table we found that as the cell area increases, the hysteresis index (HI) increases which means that the main reason for the hysteresis occurrence comes from the perovskite layer interfaces .The hysteresis less than for cells containing hole transporting layers (HTL) with Perovskite layer as reported with planar structure [16] . The measurement protocol used is voltage sweeping with scan rate 0.3mv/sec which is very slow if the scan rate increased to be 0.3v /sec, it also may reduce the hysteresis index.

5 Conclusion

For the hole - free Perovskite solar cell structure, the hysteresis decreases with the absence of the interface perovskite/HTL .Additionally ,when the area decreases, the hysteresis decreases. This ensures that the area of the interface between perovskite /TiO_2 should be small to reduce the trapping /detrapping of charges.

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