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Mixed halide perovskite light emitting solar cell

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Abstract. We demonstrate that the halide perovskite planar solar cells with the architecture of ITO/PEDOT:PSS/Perovskite/PCBM/LiF/Al show a switchable dual operation of descent photovoltaic and quite bright electroluminescence in visible range. In our experiments, the active layer is made of a mixed halide perovskite (MAPbBr₂I) and the device is properly cycled upon light and bias exposure. We argue that this curious effect of switchable double functionality between solar cell and light-emitting device in one architecture is caused by photoinduced segregation in the perovskite. It is shown that the bright red electroluminescence at low voltage of ~ 2 (3) eV appears only after cycling the device in PV regime. On the other hand, electroluminescence operation also effects the following PV mode. This effect is caused by redistribution of photoactivated ions I-/Br- and their vacancies during photoexcitation in PV regime.

1. Introduction

Solar cells (SCs) and light-emitting diodes (LEDs) may share similar structural architecture designs, but each device specifically configured energetically to provide one specific function most effectively. In SCs the positions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) of perovskite (PS) and transport layers are selected for an efficient harvesting of photogenerated electrons and holes from the PS photoactive layer to the electron transport layer (ETL) and hole transport layer (HTL) towards the contacts. At the same time, in organic or perovskite LEDs HOMO and LUMO of transport layers are selected for the efficient injection of electrons and holes into the perovskite (PS) emission layer. This difference in the device designs does not allow to create a dual functional device (SC-LED) based on conventional materials owing to the mismatch of HOMO and LUMO levels for organic LED and SC will experience additional potential barriers in the reciprocal working regime. In order to create efficient optoelectronic device with the dual functionality, one has to adjust the energy band structure of the optoelectronic device via manipulation the height and the width of the potential barriers.

In turn, halide perovskites have emerged as promising materials for optoelectronic devices development owing to their high absorption, low exciton binding energy and solution processed synthesis technology [1, 2]. These advantages allow for the cost-effective production of highly efficient solar cells (SCs) and light emitting diodes (LEDs). For the last 5 years, photovoltaic parameters of perovskite SCs enhanced and even reached efficiency values of well-established solar cell material like silicon SCs [1]. Since the perovskites possess direct band gap, they also can be used for light generation. Nowadays parameters of perovskite LEDs are among the best and these LEDs capable of concurring with LEDs based on metal-organic complexes and different conjugated polymers [2, 3]. Solution processed synthesis of perovskites allows to gradually change the band gap value in the range of 1.5 eV to 2.3 eV by the quantitative change of its halides concentration MAPbBr_xI_{3-x} (0 < x < 3) perovskite.

In turn, development of the dual functional devices are already underway, and certain progress has been achieved for the creation of such devices based on well-known material such as silicon [4] and recently emerged perovskite materials [5]. Although efficiency of obtained devices was relatively low: MAPbBr₃ perovskite based SC demonstrated ~1% PCE and 0.12% EQE_{EL}, silicon based SC demonstrated 2.1% efficiency, but it illuminated in IR region (~ 1100nm), MAPbI₃ perovskite based SC demonstrated ~12.8%



PCE and 0.04% EQE_{EL} ($\sim 750\text{nm}$) [6]. Therefore, one of the most attractive opportunities to realize the dual functional device is based on mixed halide perovskites $\text{MAPbBr}_x\text{I}_{3-x}$ ($0 < x < 3$) which will irradiate in visible range and have relatively high PCE and EQE_{EL} efficiencies. However, mixed halide perovskite exhibit one crucial property – segregation [7], which degrades device characteristics. Here we demonstrate a possibility to create such “dual functional” device and show that segregation can aid for switching of the device working regimes by p-i-n structure formation inside of the perovskite layer [8].

2. Method

Perovskite based planar p-i-n devices were fabricated in the ambient atmosphere. Design of perovskite light emitting solar cells had the following sequence of layers ITO/PEDOT:PSS/Perovskite/PCBM/LiF/Al (figure 1a) where band gap diagram is shown in the figure 1b. Device functional layers were subsequently deposited onto ITO covered substrates. Glass substrates with ITO pixels were cleaned in ultrasound bath in DI water, DMF, toluene, acetone and IPA consequently. The method of obtaining layers for these devices includes two techniques. PEDOT:PSS, perovskite and PCBM were deposited by a spin coating technique. Whereas LiF and Al were deposited by a vacuum deposition technique.

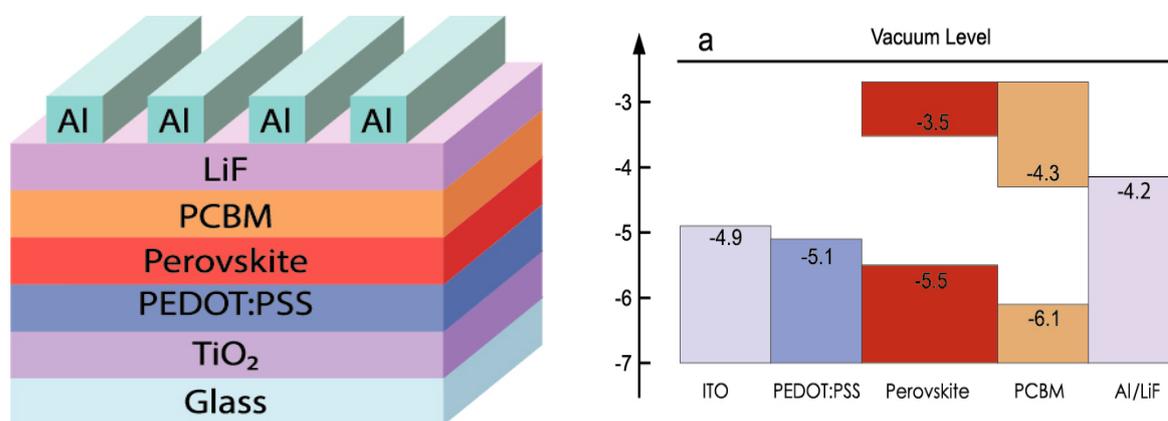


Figure 1. (a) Dual function device structure and (b) corresponding band diagram

Water dispersion of PEDOT: PSS 4083 was used as a hole transport material (HTL). It was annealed on a heating plate for 600 s at $120\text{ }^\circ\text{C}$ in ambient atmosphere. Photoactive layer based on $\text{CH}_3\text{NH}_3\text{PbBr}_2\text{I}$ was prepared by the consequent dissolving MAI and PbBr_2 in DMF:DMSO (7:3) respectively. The solutions were stirred overnight until dissolved at room temperature. Obtained perovskite solution was deposited by the single step solvent engineering technique [9] on top of HTL in 2 spin-cycles. Diethyl ether (DE) as antisolvent was slowly dripped on the rotating substrate in 10 s past the jumping from 1000 to 3000 rpm. Perovskite films were annealed on the heating plate in dry atmosphere for 600s at $100\text{ }^\circ\text{C}$. Fullerene derivative material PC_{60}BM was used as electron transport layer (ETL). PC_{60}BM was dissolved in chlorobenzene (CB) (25 mg/ml) and filtered through PTFE 0,45 syringe filter. Filtered solution was deposited onto perovskite layer by the spin coating. Before aluminium cathode deposition set of samples was divided into 2 groups. The aluminium cathode was deposited onto PC_{60}BM layer in the first group and the second group had 3nm LiF sublayer on PC_{60}BM layer. The thickness of the ETL, perovskite and HTL was measured by stylus profilometry. Acquired thickness of HTL equal 30nm, PC_{60}BM – 50nm, perovskite – 200 nm. The thickness of Al cathode was in situ controlled by Inficon deposition controller.

3. Results

We investigated influence of different working regimes on the performance of reciprocal working regime. The device was switched between PV regime and LED regime. PV regime characterized by measurement of J-V characteristics under 1 sun (AM1.5 G). LED regime characterized by application of external forward

voltage bias much higher than V_{OC} . The device demonstrated relatively good PV parameters (figure 2). In both regimes segregation will occur [10, 11] but rates of segregation will be different since regimes utilize different charge concentrations. In case of PV-regime it will manifest significantly stronger in comparison with a LED-regime, since segregation rates under 1 sun illumination usually considerably higher than in case of charge injection with equivalent density [11].

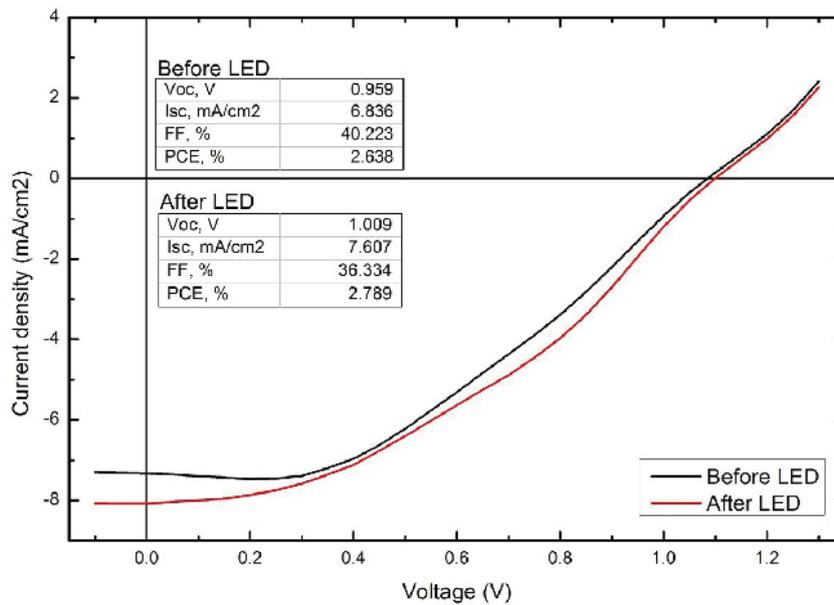


Figure 2. J-V characteristics of the device under 1 sun radiation before (black) and after (red) LED-regime

To transfer device to LED regime p-i-n structure should be created otherwise device will show weak EL and high voltage/current and eventually burn out. To ensure that p-i-n structure was formed in perovskite layer device was soaked under 1 sun illumination and at 2 Volts (figure 3a). Measured PV characteristics device was transferred into LED-regime (figure 2). Exposure device to ~2.0 V resulted in electroluminescence (LED regime) ignition (figure 3b).

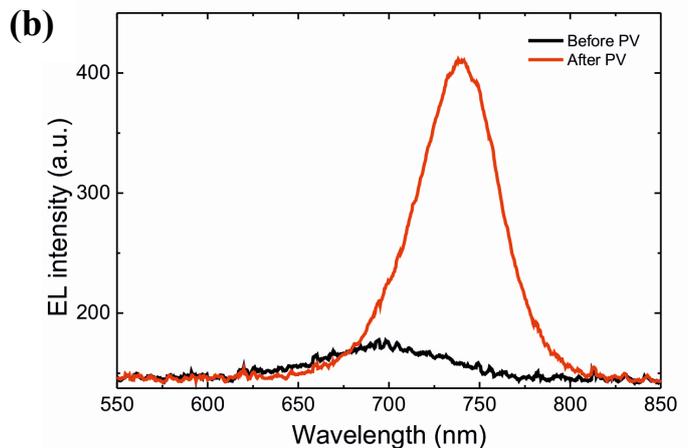


Figure 3. (a) Electroluminescence of the devices under 2V (b) corresponding intensity of the electroluminescence

The electroluminescence under 2.0 V demonstrated optical power $\sim 130 \mu\text{W}$. After the removal of external bias and device relaxation, the device was switched into the PV regime. Following PV measurements also demonstrated good PV parameters (figure 2). Cycling PV and LED regime has demonstrated the ability of the device to work in two reciprocal regimes. It should be noted, that non-soaked device demonstrated very weak EL at high voltages $\sim 4\text{V}$.

This, in turn, argues in favor of lowering potential barriers in the device band structure due to ions migration towards contacts (figure 4). Application of external voltage results in migration of ions and their vacancies generated by white light illumination towards interface layers of PS/ETL and HTL/PS. Amount of available ions and vacancies is greater than in case of the non-soaked device. Accumulation of ions and their vacancies at interface layers results in doping of interface regions of photoactive layer with following band bending and p-i-n structure formation like in case of light emitting electrochemical cells (LEECs). In LEECs light generation starts after application of high external voltage. This voltage is necessary to move ions towards contacts in polymer [12]. When p-i-n structure starts to form and potential barriers become lower, charge carriers can easier get into emission layer through potential barriers.

Segregation aids for the formation of the p-i-n structure in the device. Since it manifests in creation of photoinduced Br⁻ and I⁻ ions that tend to form enriched regions. Carriers injected into perovskite layer recombine in I-rich regions. Moreover, segregation is a temporal effect. Removal of external illumination or bias leads to backward redistribution of photoinduced ions and their vacancies.

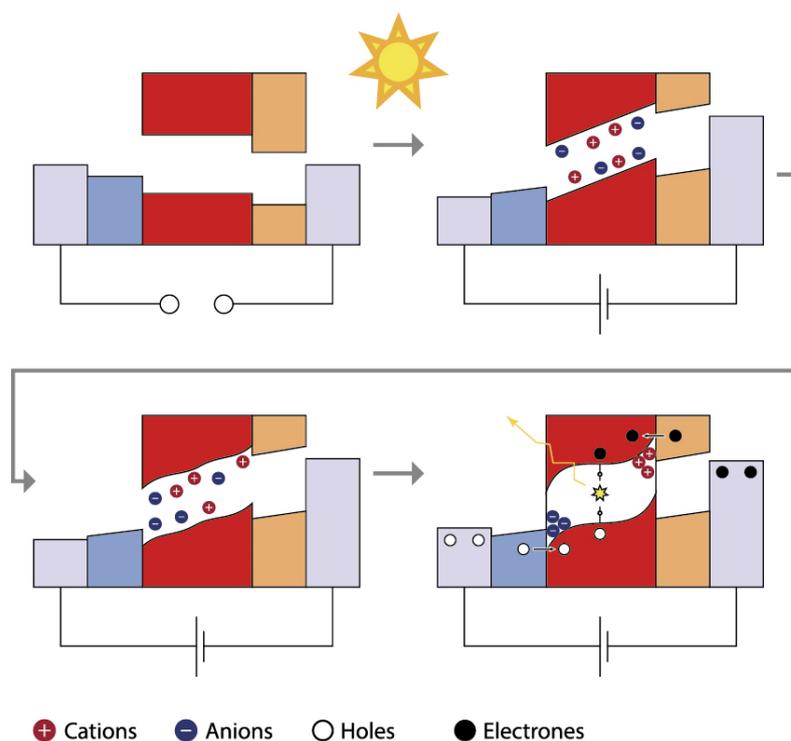


Figure 4. An example of segregation in of device structure used in present work

Further accumulation of ions and their vacancies near interfaces leads to the formation of pronounced p-i-n structure, where bent potential barriers become lower and therefore electrons and holes can easily get into perovskite layer and radiatively recombine there. Segregation and p-i-n junction formation are temporal, the removal of external bias will lead to diffusion of ions and their vacancies back to the bulk of perovskite layer (figure 4).

4. Conclusion

The work demonstrates the ability of the mixed halide perovskite optoelectronic device to work in two different regimes. In this case, segregation of halogen ions upon light irradiation, which usually negatively affects PV device performance, helps to the dual functionality by the ions movement towards the interfaces between the perovskite photoactive layer and transport layers. As a result, p-i-n structure formed within mixed halide perovskite, which allows electrons and holes to be injected into perovskite layer and radiatively recombine there in I-rich areas. The removal of external bias leads to the reduction of ions/vacancies concentration at interfaces and causes their redistribution back to the mixed halide perovskite layer, resulting in the Br- and I-rich regions dissociation.

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