

DOCTORAL THESIS

Hole extraction layer/perovskite interfacial modification for high performing inverted planar perovskite solar cells

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Abstract

Organo-metallic halide perovskite solar cells (PSCs) are considered as a promising alternative photovoltaic technology due to the advantages of low-cost solution fabrication capability and high power conversion efficiency (*PCE*). PSCs can be made using a conventional (*n-i-p*) structure and an inverted (*p-i-n*) configuration. *PCE* of the conventional *p-i-n* type PSCs is slightly higher than that of the inverted *n-i-p* type PSCs. However, the TiO₂ electron transporting layer adopted in the conventional PSCs is formed at a high sintering temperature of >450 °C. The TiO₂ electron transporting layer limits the application of conventional PSCs using flexible substrates that are not compatible with the high processing temperature. The hole extraction layer (HEL) in the inverted *p-i-n* type PSCs can be prepared by low-temperature solution fabrication processes, which can be adopted for achieving high performance large area flexible solar cells at a low cost. Inverted PSCs with a *PCE* range from 10 to 20% have been reported over the past few years. In comparison with the progresses of other photovoltaic technologies, the rapid enhancement in *PCE* of the PSCs offers an attractive option for commercial viability.

The aim of this PhD project is to study the origin of the improvement in the performance of solution-processable inverted PSCs. The surface morphological and electronic properties of the HEL are crucial for the growth of the perovskite active layer and hence the performance of the inverted PSCs. Enhancement in short circuit current density (J_{sc}), reduced loss in open circuit voltage (V_{oc}), improvement in charge collection efficiency (η_{cc}) through suppression of charge recombination were investigated systematically via controlled growth of the perovskite active layer in solution-processed inverted PSCs. Poly (3,4-ethylenedioxythiophene): poly (4-styrenesulfonate) (PEDOT:PSS) is one of the widely used solution processable conductive

materials for hole transporting in different optoelectronic devices. However, it has been reported that PEDOT:PSS HEL is related to the deterioration in the stability of PSCs due to its acidic and hygroscopic nature. Modification of PEDOT:PSS using solvent additives or incorporating metallic oxide for improving the processability and the performance of the inverted PSCs were reported. This work has been focused primary on realizing the controlled growth of perovskite active layer via HEL/perovskite interfacial modification using sodium citrate-treated PEDOT:PSS HEL and WO₃-PEDOT:PSS composite HEL. Apart from investigating the properties of the modified PEDOT:PSS HELs, the purpose of the work is to improve the understanding of the effect of modified HEL on the growth of the perovskite layer, revealing the charge recombination processes under different operation conditions, analyzing charge extraction probability, and thereby improving the overall performance of the PSCs. *PCE* of >11.30% was achieved for PSCs with a sodium citrate-modified PEDOT:PSS HEL, which is >20% higher than that of a structurally identical control device having a pristine PEDOT:PSS HEL (9.16%). The incident photon to current efficiency (*IPCE*) and light intensity-dependent *J-V* measurements reveal that the use of the sodium citrate-modified PEDOT:PSS HEL helps to boost the performance of the inverted PSCs in two ways: (1) it improves the processability of perovskite active layer on HEL, and (2) it enables to enhance the charge extraction efficiency at the HEL/perovskite interface. The suppression of charge recombination in the PSCs with a modified HEL also was examined using photocurrent-effective voltage ($J_{ph}-V_{eff}$) and transient photocurrent (TPC) measurements. Morphological and structural properties of the perovskite layers were investigated using the scanning electron microscope (SEM) and X-ray diffraction (XRD) measurements. The results reveal that high-quality perovskite active layer on the modified HEL was attained forming complete perovskite phase. The surface electronic properties of the modified PEDOT:PSS and pristine PEDOT:PSS layers were studied using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS)

measurements. XPS results reveal that treatment of sodium citrate partially removes the PSS unit in the PEDOT:PSS, resulting in an increase in the ratio of PEDOT to PSS from 0.197 for a treated PEDOT:PSS HEL to that of 0.108 for the pristine PEDOT:PSS HEL. UPS measurements also show that there is an observable reduction in the work function of the modified HEL, implying that sodium citrate-modified PEDOT:PSS HEL possesses an improved electron blocking capability, which is beneficial for efficient operation of the inverted PSCs.

The performance enhancement in MAPbI₃-based PSCs with a tungsten oxide (WO₃)-PEDOT:PSS composite HEL also was analyzed. The uniform composite WO₃-PEDOT:PSS HEL was formed on indium tin oxide (ITO) surface by solution fabrication process. The morphological and surface electronic properties of WO₃-PEDOT:PSS composite film were examined using AFM, XPS, UPS and Raman Spectroscopy. SEM images reveal that the perovskite films grown on the composite HEL had a full coverage without observable pin holes. XRD results show clearly that no residual of lead iodide phase was observed, suggesting a complete perovskite phase was obtained for the perovskite active layer grown on the composite HEL. The volume ratio of WO₃ to PEDOT:PSS of 1:0.25 was optimized for achieving enhanced current density and V_{oc} in the PSCs. It is demonstrated clearly that the use of the WO₃-PEDOT:PSS composite HEL helps to improve the charge collection probability through suppression of the charge recombination at the MAPbI₃/composite HEL interface. The charge extraction efficiency at the perovskite/PEDOT:PSS and perovskite/composite HEL interfaces were investigated by analyzing the PL quenching efficiency of the MAPbI₃ active layer. It is shown that the PL efficiency quenching at the MAPbI₃/composite HEL samples is one order of magnitude higher than that measured for the perovskite/pristine PEDOT:PSS sample, suggesting an enhanced hole extraction probability at the MAPbI₃/composite HEL interface. The combined effects of improved perovskite crystal growth and enhanced charge extraction

capabilities result in the inverted PSCs with a *PCE* of 12.65%, which is 22% higher than that of a structurally identical control device (10.39%). The use of the WO₃-PEDOT:PSS composite HEL also benefits the efficient operation of the PSCs, demonstrated in the stability test, as compared to that of the control cell under the same aging conditions.

With the progresses made in improving the performance of MAPbI₃-based PSCs, the research was extended to study the performance of efficient PSCs with mixed halide of MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃. The effect of the annealing temperature on the growth of the mixed MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃ perovskite active layer was analyzed. It was found that the optimal growth of the mixed perovskite active layer occurred at an annealing temperature of 100°C. UPS results reveal that the ionization potential of 5.76 eV measured for the mixed cation perovskite is lower than that of MAPbI₃-based single cation perovskite layer (5.85 eV), while the corresponding electron affinity of the mixed perovskite was 4.28 eV and that for the MAPbI₃ layer was 4.18 eV, respectively. The changes in the bandgap and the energy levels of the MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃ and MAPbI₃ active layers were examined using UV-vis absorption spectroscopy and UPS measurements. Compared to the MAPbI₃-based control cell, a 23% increase in J_{sc} , a 15% increase in V_{oc} and an overall 25% increase in *PCE* for the MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃ were achieved as compared to that of the MAPbI₃-based PSCs. An obvious improvement in charge collection efficiency in MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃-based PSCs operated at different V_{eff} was clearly manifested by the light intensity dependent $J-V$ characteristic measurements. PL quenching efficiency also shows the charge transfer between MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃ and PEDOT:PSS HEL is one order of magnitude higher as compare to that in the MAPbI₃-based PSCs, suggesting the formation of improved interfacial properties at the MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃/HEL interface. The impact of incorporating mixed MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃ perovskite active layer on *PCE* and the stability of the PSCs was further studied using a combination of TPC measurement and aging test. The stability of MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃-

and MAPbI₃-based PSCs with respect to the aging time was monitored for a period of >2 months. The MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃-based PSCs are more stable compared to the MAPbI₃-based PSCs aged under the same conditions. The aging test supports the findings made with the TPC and light intensity dependent $J-V$ measurements. It shows that the improved interfacial quality at the perovskite/HEL and the enhanced charge extraction capability are favorable for efficient and stable operation of MA_{0.7}FA_{0.3}Pb (I_{0.9}Br_{0.1})₃-based PSCs.

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