

Beautiful Bulk and Dynamic Interfaces of Organic-inorganic and All-inorganic Perovskite Solar Cells

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Abstract

Tunable bandgap, strong and broad absorption in the visible light, long carrier diffusion length, high defects-tolerance are excellent bulk (or single crystal) properties of hybrid perovskites that have helped perovskite PVs in making unprecedentedly fast progress. Compositional engineering and interfacial modifications have contributed remarkably to the improvement of the performance of perovskite solar cells. Some of our key findings regarding the compositional and interfacial engineering, both in organic-inorganic and all-inorganic perovskite systems, are discussed in the present article/talk.

1. Introduction

In about a decade since the pioneering work by Miyasaka et al. in 2009,[1,2] organic-inorganic lead halide perovskite solar cells (PSCs) have made rapid progress in the power conversion efficiency. A journey from about 3.5 % [1] to above 25% [3] PCE has been accomplished in a short time because of the magical properties of the hybrid perovskites. A bandgap close to 1.5 eV, which can be easily tuned by changing the component ions, strong absorption (10^5 cm^{-1}) in a broad range (800- 400 nm) in the visible spectrum, long carrier diffusion length, and defects-tolerance nature of perovskites work excellently in PV devices. The beauty of the perovskite materials (ABX_3) is that they can be chemically modified easily by changing the type and concentration of either of the A, B, or X ions. Compositional engineering of the perovskite [4,5] and interfacial engineering [6,7] of different stacking layers in the device have played pivotal roles in the accomplishment of both high power conversion efficiency and longer stability. In general, while compositional changes in the perovskite alter the optical bandgap, film morphology, and therefore the photovoltaic performance, interfacial modifications improve cell performance by improving the carrier dynamics at the interfaces. Indeed, a lot of work has been reported on interfacial modifications and their effect on cell efficiency, current-voltage hysteresis, and stability. Any chemical or physical change at the perovskite/ETL, perovskite/HTL (hole transport layer) interface alters the performance. Although perovskite/HTL interface is the beating heart of PSCs and modification of this interface has been witnessed to produce excellent results in terms of improved PCE and stability, the perovskite/ETL interface plays an equally important role in improving the performance by suppressing interfacial carrier recombination and shifting the energy levels for efficient carrier collection. As TiO_2 is the most widely used ETL, a great amount of work

has been done on modification of the TiO_2 either by surface treatment or doping. Varieties of materials have been used for surface modification of TiO_2 which have enhanced the PCE and stability of PSCs. Some of our findings regarding the composition, morphology, and interfaces in the PSCs are discussed below/will be discussed during the talk.

2. Results and discussion

Large grains with fewer grain boundaries help in improving the performance by minimizing non-radiative recombination losses. Hence, the crystallization process of perovskite is the most critical step in device fabrication. A stark difference in the morphology of perovskite (MAPbI_3) film and cell performance can be observed just by changing the crystallization process from conventional annealing to antisolvent method. The triple cation (MA, FA, Cs) based perovskites prepared in controlled humidity can work with PCE >20%. While in the majority of cases, it seems the reducing the grain size can minimize recombination, grain boundary passivation can be also accomplished by suitable functional materials. In one of our studies, we found that germanium doping into double cation mixed halide perovskite $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}_{1-x}\text{Ge}_x(\text{I}_{0.9}\text{Br}_{0.1})_3$ can result in improved efficiency by reduced recombination. The champion cells, in this case, were found to work with an efficiency of 22.09%.

As another major activity in the group, we have also investigated the role of interfaces in performance improvement and stability. While hysteresis was a concern in the beginning years (2013-2014) and was being assumed to be arising from the ferroelectric property of hybrid perovskites, we found that it is instead originated from the carrier dynamics at the interfaces. A lot of work has been reported on the interfacial modification to reduce/eliminate hysteresis. In most of the cases, the improved performance has been attributed to either improved coverage, or perovskite film morphology and crystallinity, or better interfacial contact, or passivation of defects. Besides, energy level shifting and band alignment caused by interfacial modification is another important player in device performance.

Our observations in a recent study [9] were that a TiO_2 ETL modified with Cesium acetate (CsAc) did not show any change in perovskite morphology but formed a PbI_2 -rich interface in the TiO_2 -CsAc case. The cell performance improved through the formation of a PbI_2 -rich composition at $\text{MAPbI}_3/\text{TiO}_2$ interface which is more n-type and down-shifts the CB level of MAPbI_3 at the interface, helping in better carrier transfer at the interface (Figure 1). Interfaces not only influence J-V hysteresis and overall efficiency, but

it also impacts the device stability significantly. In a study on the thermal stability of MAPbI₃ solar cells, we found that spiro-OMeTAD (widely used as a hole transporting material) plays a notorious role in the performance deterioration of the cells at elevated temperatures. It seems that not the degradation of perovskite (MAPbI₃) but some physical/chemical alteration at the perovskite/spiro-OMeTAD interface is the main reason for performance degradation in the MAPbI₃ cells.

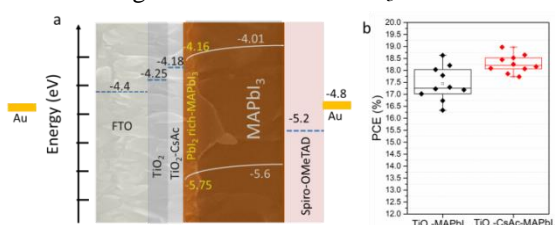


Fig. 1 (a) Schematic diagram showing band level shifts of MAPbI₃ and TiO₂ by CsAc surface modification, (b) PCE of PSCs with TiO₂ and TiO₂-CsAc ETLs. [9]

Recently, compositional engineering and interfacial modification have also become popular and produced good results in all-inorganic perovskites (CsPbX₃). First, the formidable problem with all-inorganic CsPbI₃ perovskites is the stabilization of its black photoactive phase, which is otherwise formed at temperature > 300 °C, at ambient RT conditions. In an early study, we found that doping CsPbI₃ with Eu (Eu²⁺ or Eu³⁺) can form the black phase at lower temperatures and showed reasonable stability. Unlike, CsPbI₃, CsPbI₂Br crystallizes in a black phase at RT but the performance and stability of CsPbI₂Br cells seem to suffer from recombination losses inside the film and at the interfaces. Addressing this issue, we followed an additive approach to passivate defects in the CsPbI₂Br film. Lead propionate, used as an additive in the CsPbI₂Br precursor, was found to improve the performance and environmental stability, and the cells at best conditions performed with an efficiency of > 14.5%. Another interesting fact came out through a recent study [10] that V_{oc} loss in CsPbI₂Br cells can be largely contributed from interfacial recombination. A simple method of producing a SnO_x amorphous ETL happened to improve the V_{oc} significantly. Aging of SnCl₂ precursor solution that changed the properties of the SnO₂ ETL in favor of the minimization of Voc loss, resulted in devices with V_{oc} > 1.4 V and PCE = 15.5% (Figure 2)

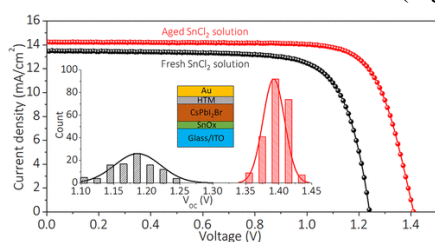


Fig. 2 Comparison of J-V curves and V_{oc} of CsPbI₂Br solar cells made with SnO₂-SnO_x bilayer ETL prepared from fresh and aged SnCl₂ solution. [10]

3. Conclusions

The excellent bulk (single crystal) properties of hybrid perovskites and easy chemical manipulation of the materials through solution processes have helped PSCs to make rapid progress in PCE. Composition and interfacial engineering have played huge roles in improving cell performance and stability. In our observations during some of our studies, we have found that suppressing recombination losses by germanium doping of FA-M- based perovskites, use of lead propionate in all-inorganic CsPbI₂Br and SnO₂/CsPbI₂Br interfacial modification by aged SnCl₂ solution improves the PCE and stability of the cells.

Acknowledgments

The research works being discussed here have been supported by JST (ALCA), and the Japanese Society for Promotion of Science (JSPS) (Grant-in-Aid for Scientific Research S). The authors acknowledge Professor H. Segawa for giving access to research facilities at the Research Center for Advanced Science and Technology (RCAST), The University of Toyo.

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