

Compositional and interfacial engineering for high performance perovskite solar cells

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Halide perovskite-based photovoltaic (PV) cells have been developed with various compositions of perovskite materials as solution processable semiconductors.¹ The power conversion efficiency (PCE) of perovskite solar cells (PSCs) have reached beyond 25%; the record value competes the top PCE of crystalline Si cells. In the design of PSCs, carrier transport materials and their contacts with perovskite layers are important elements in determining the PV performance. Metal oxide mesoporous layers (<200 nm) such as TiO₂ and SnO₂ are widely employed as electron transport layers (ETLs) and their interfaces with perovskite crystals play a significant role in improving the PV performance. In particular charge recombination loss at the interface leads to reduction in voltage output (open-circuit voltage, V_{OC}) and PCE. To minimize the recombination loss, ETL is usually combined with a thin non-porous hole-blocking layer (HBL) covering the electrode substrate. Modification of the electrode surface with ultra-thin organic or inorganic materials as a dense compact HBL is prerequisite to ensure high V_{OC} and PCE. In addition to HBL, various organic or inorganic molecules as dopants can function to passivate the chemical and physical defects existing at junction interfaces and grain boundaries of perovskite crystals.¹ Such passivation also leads to enhance V_{OC} and PCE. These interfacial modification and molecular passivation methods tend to suppress the generation of hysteresis in current-voltage (J-V) characteristics as a result of well-balanced electron/hole transports.

For hybrid multi-cation perovskite, FA_{0.83}MA_{0.17}Pb (I_{0.9}Br_{0.1})₃ (FA=formamidinium, MA=methylammonium), ~3% doping of Ge ion to Pb was found to passivate the grain boundary surface of perovskite and interface of perovskite and hole transport layer (HTL). Based on this passivation, we could enhance the V_{OC} of the device up to 1.18V with PCEs over 22%.² For the purpose to improve the ETL and perovskite interface, thin films (<10 nm) of amorphous metal oxides such as TiOx and SnOx are effective in creating a void-less compact interlayer to connect ETL and perovskite. They also block hole injection and minimize recombination to enhance V_{OC}. In fabrication of all-inorganic CsPbI₂Br-based planar photovoltaic cells, we modified the surface of SnO₂ ETL with an amorphous SnOx (<5 nm) as an interlayer at the contact of CsPbI₂Br layer. Using a hole-transport layer (HTL) composed of a dopant-free copolymer (poly(DTSTPD-r-BThTPD)), the CsPbI₂Br device yielded a power conversion efficiency of 17% with a high V_{OC} reaching 1.42V (Fig. 1).^{3,4} A reference device without the SnOx interlayer gave a poor J-V performance with a large hysteresis and a low Voc (<1.2V), indicating the essential role of the interlayer. Another example of inorganic passivator is MXene, a 2D layered molecular material comprising Ti₃C₂. We treated a colloidal solution of MXene by oxidation to form nanosheets of HO-Ti₃C₂T_x, which show semiconductivity suitable for ETL. Thin layer (<20 nm) of the oxidized MXene works as a good ETL in a planar device with efficiency over 18%.⁵ Efficiency reaches more than 20% when HO-Ti₃C₂T_x is hybridized with SnO₂, which chemically interacts HO-Ti₃C₂T_x via oxygen bonding. Being mechanically and thermally robust, MXenes are promising nanomaterials to modify the function of heterojunction interfaces. Organic small molecules also serve as modulators to passivate the defects at the junction interface. Among various molecules, we found that an organic peroxide, artemisinin (water-insoluble anti-malarial drug), works to modify the interface of SnO₂ ETL and multi-cation perovskite (Rb_{0.05}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.9}Pb(I_{0.95}Br_{0.05})₃).⁶ This redox-active molecule is considered to interreact with the oxide surface and lead cation in passivation process. Artemisinin-based passivation was applied to the SnO₂-perovskite interface of a plastic film flexible PV device. The flexible device showed decreased hygroscopicity due to the effect of artemisinin, leading to an increase in shelf life. Its effects of enhancing V_{OC} improved the device efficiency up to 21.1% with V_{OC} of 1.13V; the efficiency is the highest value ever achieved for plastic perovskite PV device. All of the above

inorganic and organic passivators are chemically and thermally stable non-ionic materials and inactive against their diffusion. Such properties will guarantee structural stability of ultra-thin hole-blocking interlayers involved in defect passivation.

Our challenge to create the method of defect passivation by compositional engineering and improvement of solution process is in progress.

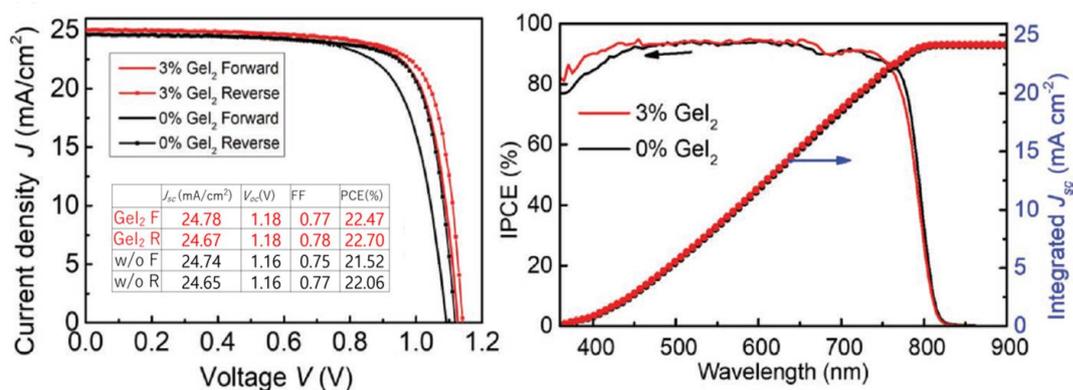


Figure 1. Efficiency enhancement of multi-cation perovskite (FA_{0.83}MA_{0.17}Pb (I_{0.9}Br_{0.1})₃) photovoltaic cell by doping GeI₂ as a passivator of perovskite crystals; J-V characteristics (left) and incident photon to current quantum efficiency (IPCE) action spectra (right).

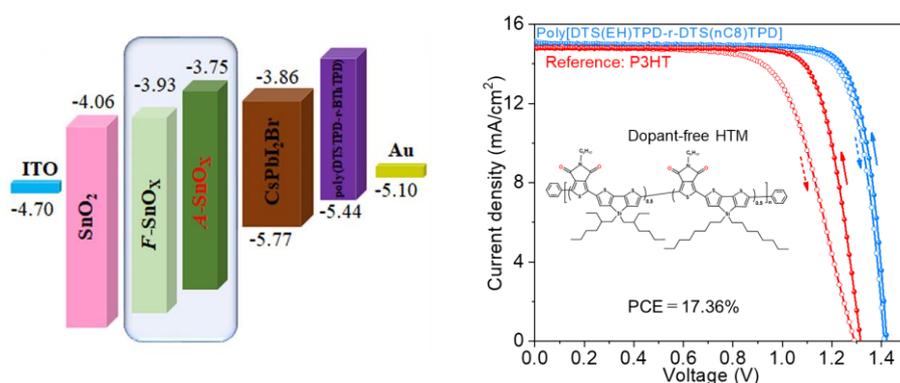


Figure 2. Voc and efficiency enhancement in all-inorganic perovskite (CsPbI₂Br) by using amorphous SnO_x composing double layer of mesoporous SnO₂ and SnO_x; device structure (left) and J-V performances of reference device (using P3HT as HTL) and dopant-free copolymer-based device (right).

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Biography



Tsutomu (Tom) Miyasaka received his Doctor of Engineering from The University of Tokyo in 1981. In 2001, after 20 year R&D work at Fuji Photo Film, Co., he moved to Toin University of Yokohama (TUY), Japan, as professor in Graduate School of Engineering, where he served as the dean of Graduate School (2006–2009). In 2004 he has established a TUY-based company, Peccell Technologies, serving as CEO. In 2005 to 2010 he also served as a guest professor at The University of Tokyo. Currently he is a professor of TUY and a fellow of Research Center for Advanced Science and Technology (RCAST) of The University of Tokyo. His research has been focused on the study of light to electric energy conversion involving photochemical processes by enhancing rectified charge transfer at photo-functional interfaces of semiconductor electrodes. He has contributed to the design of low-temperature solution-printing process for fabrication of dye-sensitized solar cells and solid-state hybrid photovoltaic (PV) cells. Since the discovery of the organic inorganic hybrid perovskite as PV material in 2006 and fabrication of high efficiency PV device in 2012, his research has been focused on R&Ds of the halide perovskite PV device. He was awarded a Ministry of Science & Education prize in 2009 on his green sustainable solar cell technology. In 2017 he received Chemical Society of Japan (CSJ) Award and Clarivate (Thomson Reuter) Citation Laureate in 2017 on his research of perovskite photovoltaics. He is presently directing national research projects funded by Japan Science and Technology Agency (JST) and Japan Aerospace Exploration Agency (JAXA).