

A HIGHLY EFFICIENT PEROVSKITE SOLAR CELLS VIA IMPROVED CARRIER MANAGEMENT

Gabkyung Seo¹, Jason J. Yoo² and Seong Sik Shin^{3*}

¹ Department of Energy Science, Sungkyunkwan University, Suwon, Korea

² Division of Advanced Materials, Korea Institute of Chemical Technology, Daejeon, Korea

³ Department of Nano Engineering, Sungkyunkwan University, Suwon, Korea
Insert E-mail address

¹ gabkyung91@skku.edu

² jasonyoo@kriect.re.kr

³ sss85@skku.edu

Since the Industrial Revolution began around 1750, with significant increases in consumption of fossil fuels like coal and oil, humanity has faced serious problems such as climate change, rise in global temperatures, changes in the ecosystem of earth, and rising sea levels due to greenhouse gases (e.g., carbon dioxide) generated from burning fossil fuels for electricity and heat. Renewable energy offers the advantage to counteract issues of the negative impact on the environment, and countries around the world are actively developing renewable energy technologies to reduce greenhouse gas emissions.

Renewable energy is a sustainable and inexhaustible energy source, unlike finite fossil fuels. It also reduces carbon dioxide pollution and has a lower environmental impact. Among various renewable energy sources, solar energy is considered as a one of promising renewable energy source because it is clean and inexhaustible and abundant and provides as much as 10,000 times the energy consumed by human beings. Solar energy can be converted into electricity using photovoltaic (PV) devices. Among these devices, perovskite solar cells (PSCs) have made significant breakthroughs in the PV field.

The last decade has seen a rapid and remarkable rise in the power conversion efficiency (PCE) of PSCs, accompanied by a considerable maturation of their scientific and technological basis. Such remarkable progress motivates both the exploration of new methods to advance the PCE of PSCs towards their theoretical efficiency limit as well as a deep interest in a fundamental understanding of their remarkable performance and present efficiency limitations. The efficiency limit, determined by detailed balanced theory, places a ~33% theoretical upper bound for the PCE of single junction solar cells. Approaching this efficiency limit is challenging, especially for emerging technologies such as PSCs, as only Silicon (Si) and Gallium Arsenide (GaAs) cells show PCEs surpassing 80% of their efficiency limit. As a result, understanding the efficiency bottleneck for PSCs and developing strategies to overcome limiting factors is crucial.

For the best performing PSCs, their short-circuit current density (J_{SC}) already closely approaches the theoretical limit. However, the fill factor (FF) and the open-circuit voltage (V_{OC}) deficit, defined as the radiative V_{OC} limit (V_{OC}^{rad}) minus V_{OC} , have remained bottlenecks towards further approaching the theoretical efficiency limit. Improvements in carrier management, which is closely tied to the FF and the V_{OC} , is thus the more obvious path to increase the device performance of PSCs. Strategies need to be developed to: 1) efficiently extract photo-generated carriers from the photo-absorber, and 2) transport these carriers through the transporting layer without carrier recombination and photo-voltage losses. The external electroluminescence quantum efficiency (EL_{EQE}) of a PV device, determined by measuring the luminescence efficiency under forward bias, is a direct measure of the radiative efficiency of carrier recombination. The EL_{EQE} can be used to

quantify the non-radiative contribution to the V_{OC} deficit via the reciprocity theorem, and is a useful metric for solar cell characterization.

Tin dioxide (SnO_2) based electron transport layer (ETL) have gained much interest as they offer favorable band alignment, while being low temperature processable. Among various deposition methods, SnO_2 nanoparticle (NP) based ETL have demonstrated the best performances thus far. However, SnO_2 NP based PSCs exhibit relatively low EL_{EQE} 's, and thus higher V_{OC} deficits, compared to TiO_2 based PSCs, in spite of various efforts to eliminate non-radiative recombination pathways. These deficiencies motivate developing strategies that minimize photo-voltage losses at the ETL/perovskite interface so as to minimize the V_{OC} deficit, thus encouraging the search for a different deposition method that can develop the full potential of SnO_2 ETLs. The ideal SnO_2 ETL will generate high photo-voltage and FF by having a complete and conformal coverage without pinholes, an ideal band alignment to efficiently extract electrons while blocking hole back-transfer, a low defect density to prevent detrimental interface recombinations, and be thin enough to promote efficient charge extraction.

In this study, we report a holistic approach to improving the performance of PSCs through charge carrier management. For that, we focused on developing a high-quality of SnO_2 ETL by chemically tuning its physical and electrical properties via chemical bath deposition (CBD). The CBD method offer advantages for synthesizing high-quality ETLs with uniform and complete coverage [1]. However, a lack of understanding of the complex chemical CBD reactions has prevented the fabrication of highly efficient PSCs. To solve current issues, we focused on the understanding of CBD reaction mechanism. we found out that the type of Sn intermediate species change depending on the pH of the reaction solution due to the hydrolysis reaction of the Sn^{2+} precursor (SnCl_2). Concurrently, as the SnO_2 formation reaction progresses, dissolved oxygen is depleted and a limited oxidation reaction of metal ions occurs. Furthermore, these changes significantly affected the chemical composition, the electronic properties, and the density of oxygen vacancy (V_{OX}) defect of the final SnO_2 film. More specifically, the Sn^{2+} ions dissolved in strong acidic aqueous solution form $\text{Sn}(\text{OH})^+$ intermediate species as a result of a hydrolysis reaction. Subsequently, $\text{Sn}(\text{OH})^+$ is then oxidized to Sn^{4+} by the dissolved oxygen in the solution. The Sn^{4+} ions then react with OH ions in water to form $\text{Sn}(\text{OH})_4$ species, which are finally converted to SnO_2 via a dehydration reaction. But, due to a sharp decrease in oxygen dissolved in the reaction solution, nonstoichiometric SnO_{2-x} is synthesized. When the reaction further proceeds and pH of solution reaches to neutral range, a different Sn intermediate species, $\text{Sn}_3(\text{OH})_4^{2+}$, forms in the reaction. The $\text{Sn}_3(\text{OH})_4^{2+}$ intermediate species can undergo a condensation reaction when the pH is sufficiently high, resulting in $\text{Sn}_6\text{O}_4(\text{OH})_4$. The $\text{Sn}_6\text{O}_4(\text{OH})_4$ is then partially transformed to SnO via a dehydration reaction, producing a mixture of $\text{Sn}_6\text{O}_4(\text{OH})_4$ and SnO .

Based on this, we successfully modulated the physical and electronic properties of the SnO_2 ETL, resulting in high-quality SnO_2 ETLs with excellent coverage and low V_{OX} density while preventing the formation of unwanted secondary crystal phases. As a result, transient photovoltage (TPV) and time-resolved photoluminescence (TRPL) results show that PSCs with the developed SnO_2 ETL show a reduction in non-radiative recombination. As a result, PSCs using the developed SnO_2 ETL exhibit an improved average PCE of approximately 24%. And, further optimization of the perovskite layer increased the PCE up to 25.2%, which translates to 80.5% of the SQ limit for its band gap.

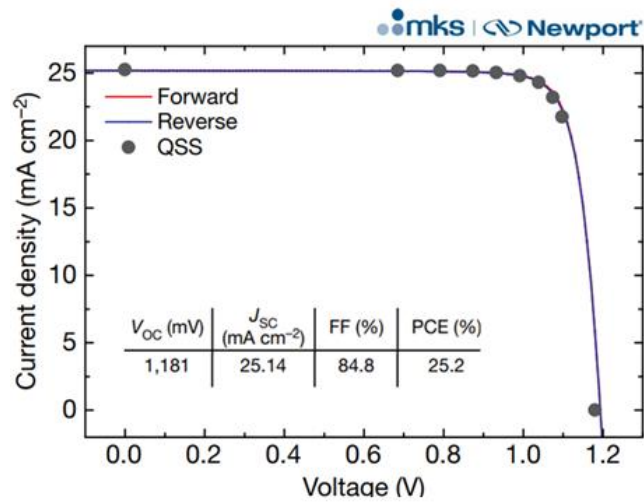


Figure 1. J-V curves of the champion device.

Reference

[1] Anaraki, E. H., Kermanpur, A., Steier, L., Domanski, K., Matsui, T., Tress, W., Michael Saliba, Michael Grätzel, Michael Grätzel & Correa-Baena*, 2016, Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide, Energy & Environmental Science 9, 10, 3128-3134.