

Understanding the degradation mechanisms of organic-inorganic halide perovskite solar cells

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論 文 内 容 の 要 旨

Developing a highly efficient, stable and cheap solar cell technologies is of great interest for establishing an environmental-friendly society with zero carbon dioxide emission. One of the most promising technologies is organic-inorganic lead halide perovskite solar cells (PSCs), which were firstly developed by the research group of Professor Tsutomu Miyasaka in 2009. PSCs, which can be fabricated with cost effective simple solution processing, have already demonstrated the highest certified power conversion efficiency (PCE) of 25.2% which is comparable to commercially available silicon solar cell technology. However, the long-term operational stability of PSCs is still low, thus hindering the commercialization of this technology. It is known that the PSCs degrade easily upon exposure to oxygen, moisture, heating and light illumination. In addition, electric field induced ion migration accelerates the degradation of PSCs. Oxygen and moisture induced extrinsic degradation issues are possible to solve by using a suitable encapsulation technology. Therefore, in this thesis, I studied degradation mechanisms of PSCs, which are associated with light illumination, ion migration and heating. By understanding and overcoming the PSC degradation, I was able to greatly improve the long-term stability at room and high temperature.

In **Chapter 1**, I described the general introduction of perovskite materials and PSCs. Firstly, I described the structures and properties of materials. Then, I discussed working principle, device architecture, progress of development, and open questions of PSCs. Lastly, I described aims and outline of the thesis.

In **Chapter 2**, I studied the light induced degradation mechanism of PSCs by changing the stoichiometry of perovskite materials. In a perovskite precursor solution used for spin-coating, excess lead iodide (PbI_2) has often been used to obtain higher-quality perovskite films for higher-performance PSCs. However, how excess PbI_2 affects the long-term stability of PSCs under light illumination has been rarely studied. Therefore, I investigated the influence of excess PbI_2 on the light induced degradation of PSCs. I found that unreacted excess PbI_2 crystals tend to form in films when the PbI_2 concentrations in precursor solutions increase. While the PCEs of all PSCs were similar and were not strongly correlated with the PbI_2 content, the solutions with higher concentrations of PbI_2 produced PSCs with accelerated degradation. This degradation was related to the decomposition of PbI_2 into metallic lead and iodine under

light illumination.

In **Chapter 3**, I studied ion migration induced degradation of PSCs. Because of the ionic character of halide perovskite materials, the ion migration through the perovskite absorber layer of PSCs during operation is a potential obstacle for efficient and stable solar power conversion. I found that the presence of hydroxyl groups ($-\text{OH}$) on an electron-transporting layer (ETL) of SnO_2 accelerates the ion migration and induces the ionic localization at the ETL surface. To avoid the localization of ions, I deactivated the hydroxyl groups by chemically modifying the SnO_2 surface with a self-assembled monolayer (SAM). Introducing this interfacial SAM significantly improved the long-term stability. With this SAM treatment, I obtained almost no degradation of PSCs at room temperature under continuous illumination for 1,000 hours.

In **Chapter 4**, I studied a degradation mechanism of PSCs at high temperature. Most of high-performing PSCs reported to date contain a small molecular hole transporting layer (HTL) material of 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD). However, the stability of PSCs with spiro-OMeTAD at high temperature is known poor. I found that post-doping of spiro-OMeTAD by iodine diffused from the perovskite layer is a feasible reason for the degradation of PSCs at a high temperature of 85 °C. The highest occupied molecular orbital (HOMO) level of the spiro-OMeTAD layer changed from -5.3 to -5.8 eV by the iodine doping, which led to the formation of a hole extraction barrier with the perovskite layer having the valence band maxima of -5.5 eV. When I inserted an iodine-blocking layer between the spiro-OMeTAD layer and the perovskite layer or replaced the iodine-containing perovskite layer with an iodine-free (bromine-based) perovskite layer, I obtained better stability at high temperature, because of the suppressed iodine doping into spiro-OMeTAD.

In **Chapter 5**, I concluded the thesis and proposed the future perspective. I described main findings of each chapters, and I discussed the study plan in the future. Although, I achieved very stable PSCs for 1,000 hours at room temperature, the estimated lifetime, at which efficiency decreases to 80% of the initial, of my PSCs is $\sim 13,000$ h. This value roughly corresponds to 1.5 years. Therefore, it is required to continue the degradation studies at room temperature to provide ~ 20 years of stable PSCs required for practical use. In addition, measuring the stability of PSCs with accelerated testing methods such as under concentrated sun light would be helpful to estimate stability of very long duration. Furthermore, to increase the stability of PSCs at high temperature, developing a method to stop iodine evacuation or developing a new HTL material that should be chemically stable to detrimental iodine gas is highly demanded.