

# Preparation of Purified Key Materials for Lead and Tin-based Perovskite Solar Cells

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## Abstract

Metal halide ABX<sub>3</sub> perovskites are highly attractive as a light harvesting material in next generation photovoltaics. Improved materials and fabrication methods has led to the development of perovskite solar cells with power conversion efficiencies (PCE) exceeding 20%. In this presentation, we introduce our purified perovskite precursor materials, and show how they lead to increased efficiency in both lead and tin-based perovskite solar cells.

## 1. Introduction

Metal halide perovskites have attracted considerable attention for use in next generation photovoltaic applications. Polycrystalline perovskite layers can be fabricated by solution methods at low temperature, making the materials ideally suited for the development of light and flexible solar panels. The power conversion efficiency of perovskite solar cells has increased rapidly to more than 20%, and the current record now stands at 25.2%. Such impressive progress can be attributed to a number of factors, including improvements of the perovskite fabrication methods, compositional refinements made to the perovskite formula, and increased purity of the perovskite precursor materials. Our research on perovskite solar cells focuses on the development of highly purified perovskite precursor materials[1-4], improved solution fabrication methods for the perovskite layers[5-7], as well as the design and synthesis of new organic semiconductors for the charge-collecting layers[8-15]. In this presentation, we will introduce our results on lead and tin-based perovskite solar cells.

## 2. Results and discussion

### Purified PbI<sub>2</sub>

PbI<sub>2</sub> is a key precursor for perovskite materials. Our first contribution to this field was the development of purified PbI<sub>2</sub> starting material [1]. Up until 2014 - the early days of research on perovskite solar cells – devices generally suffered from poor reproducibility owing to the highly variable quality of the fabricated perovskite layers. We found that, despite a listed trace metal basis purity of 99.999%, commercially available PbI<sub>2</sub> contained about 2000 ppm of water, and further that this water was the leading cause for the variable quality of the perovskite (Fig. 1a). Fortunately, PbI<sub>2</sub> can be purified by simple distillation. We showed that purified PbI<sub>2</sub> is essential for achieving highly efficient and reproducible perovskite solar cells (Fig. 1b). Our purified PbI<sub>2</sub> was commercialized by Tokyo Chemical Industry (TCI) and is now widely used as a standard precursor material all over the world.

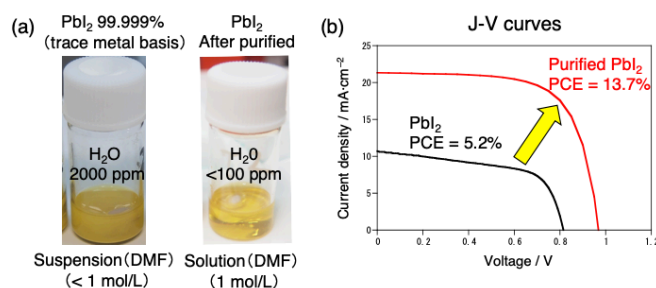


Fig. 1 The effects of purified precursor materials (PbI<sub>2</sub>): a) Comparison of conventional and purified PbI<sub>2</sub> b) Photovoltaic performance of perovskite solar cells using purified PbI<sub>2</sub>.

### Second and third generation precursor materials MAPbI<sub>3</sub>·DMF and FAPbI<sub>3</sub>·2DMF

To further improve the fabrication process of perovskite layer for higher efficiency of perovskite solar cells, we synthesized MAPbI<sub>3</sub>·DMF [2] and FAPbI<sub>3</sub>·2DMF complex [3] as second and third generation purified precursor materials for perovskite, respectively. The wider process window was realized by the use of MAPbI<sub>3</sub>·DMF, which facilitated the fabrication of large area devices, as demonstrated by our 22.0 cm<sup>2</sup> module, eight-cell module with >8.6V high output voltage (1.08 V/cell, Fig. 2a) [2]. The third-generation material, FAPbI<sub>3</sub>·2DMF, is a suitable precursor for FA-rich mixed composition perovskite. When combined with a SnO<sub>2</sub> electron collecting layer, devices with high PCE > 20% could be fabricated at low temperatures below 150 °C (Fig. 2b) [3].

### Perovskite solar modules

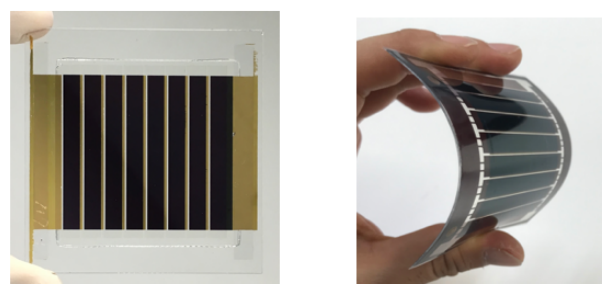


Fig. 2 Perovskite solar modules fabricated using second generation precursor material, MAPbI<sub>3</sub>·DMF, on glass or film substrate.

### Precursor materials for tin-based perovskite solar cells

While the performance of lead-based perovskite solar cells and modules has reached a very high level, the use of lead remains a significant impediment to commercialization. Replacing lead with more environmentally friendly elements, such as tin or bismuth, is therefore an essential challenge for

the next phase of perovskite research and development. The unique challenges for Sn-based perovskites include facile oxidation of divalent Sn(II) into Sn(IV) and unusually poor film morphology. Tin oxidation is the cause of very poor PCE numbers for tin-based devices, as electrical traps created by Sn(IV) in the perovskite crystal structure lead to increased charge carrier recombination. Problems with the film morphology, including imperfect coverage of the perovskite layer on many oxide and organic surfaces, can be largely viewed as a problem of crystallization control.

To address these issues, we developed a series of purified precursor materials, including  $\text{SnI}_2(\text{dmf})$ ,  $\text{SnBr}_2(\text{dmf})$ , and  $\text{SnCl}(\text{dmf})$  [4]. The inclusion of bound solvent molecules help stabilize the materials, leading to improved shelf life. In addition, a unique fabrication protocol was developed to control the crystal growth and improve the film morphology in a two-step process, where Hot Antisolvent Treatment (HAT) is combined with Solvent Vapor Annealing (SVA) [6]. With this methods, tin-based perovskite devices with PCE >7% were obtained as a result of the improved topographical and electrical qualities of the perovskite layer.

To address the significant issue of oxidation of the Sn(II) species during the preparation stage, we recently developed a novel scavenger method for removing Sn(IV) from the precursor solution (Fig. 3) [7]. Using *in situ* Sn(0) nanoparticle treatment, Sn(IV)-free Sn-based perovskites could be realized for the first time. With the aid of this scavenger method, Sn-based solar cells reaching a PCE of 11.5% (certified 11.2%) were demonstrated.

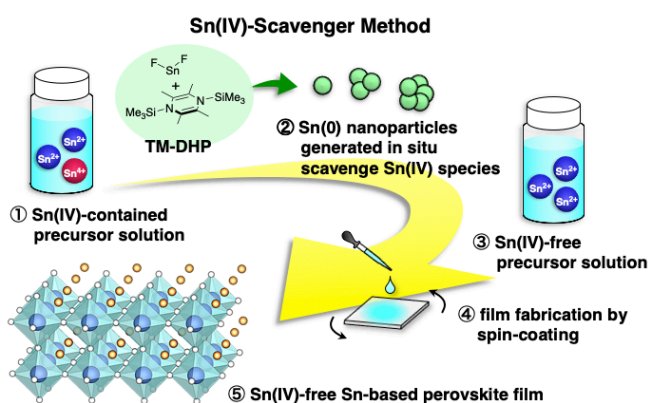


Fig. 3 Schematic illustration for Sn(IV) scavenger method using *in situ* Sn(0) nanoparticle treatment.

## Acknowledgements

We would like to express sincere thanks to the collaborators, all the students and researchers in my group, Drs. R. Murdey, T. Nakamura, M. A. Truong, M. Ozaki, J. Liu, T. Handa, F. Wang, Profs. Y. Kanemitsu, H. Ohkita, K. Matsuda at Kyoto University. We also appreciate Drs. T. Tanabe, I. Ikada, and H. Nishimura at Tokyo Chemical Industry (TCI). This work was partially supported by JST-ALCA (JPMJAL 1603), JST-COI (JPMJCE 1307), JST-CREST (JPMJCR16N3) programs, NEDO, International Collaborative Research Program of ICR, Kyoto University.

## References

- [1] A. Wakamiya, M. Endo, T. Sasamori, N. Tokitoh, Y. Ogomi, S. Hayase, Y. Murata, *Chem. Lett.* **2014**, 43, 711.
- [2] M. Ozaki, A. Shimazaki, M. Jung, Y. Nakaike, N. Maruyama, S. Yakumaru, A. I. Rafieh, T. Sasamori, N. Tokitoh, P. Ekanayake, Y. Murata, R. Murdey, A. Wakamiya, *Angew. Chem., Int. Ed.* **2019**, 58, 9389.
- [3] M. Ozaki, Y. Ishikura, M. A. Truong, J. Liu, I. Okada, T. Tanabe, S. Sekimoto, T. Ohtsuki, Y. Murata, R. Murdey, A. Wakamiya, *J. Mater. Chem. A* **2019**, 7, 116947.
- [4] M. Ozaki, Y. Katsuki, J. Liu, T. Handa, R. Nishikubo, S. Yakumaru, Y. Hashikawa, Y. Murata, T. Saito, Y. Shimakawa, Y. Kanemitsu, A. Saeki, A. Wakamiya, *ACS Omega* **2017**, 2, 7016.
- [5] M. Ozaki, Y. Nakaike, A. Shimazaki, M. Jung, N. Maruyama, S. Yakumaru, A. I. Rafieh, P. Ekanayake, T. Saito, Y. Shimakawa, T. Sasamori, Y. Murata, R. Murdey, A. Wakamiya, *Bull. Chem. Soc. Jpn. (Materials Innovation)* **2019**, 92, 1972.
- [6] J. Liu, M. Ozaki, S. Yakumaru, T. Handa, R. Nishikubo, Y. Kanemitsu, A. Saeki, Y. Murata, R. Murdey, A. Wakamiya, *Angew. Chem., Int. Ed.* **2018**, 57, 13221.
- [7] T. Nakamura, S. Yakumaru, M. A. Truong, K. Kim, J. Liu, S. Hu, K. Otsuka, R. Hashimoto, R. Murdey, T. Sasamori, H. D. Kim, H. Ohkita, T. Handa, Y. Kanemitsu, A. Wakamiya, *Nat. Commun.* **2020**, 11, 3008.
- [8] H. Nishimura, N. Ishida, A. Shimazaki, A. Wakamiya, A. Saeki, L. T. Scott, and Y. Murata, *J. Am. Chem. Soc.* **2015**, 137, 15656.
- [9] M. A. Truong, J. Lee, T. Nakamura, J.-Y. Seo, M. Jung, M. Ozaki, A. Shimazaki, N. Shioya, T. Hasegawa, Y. Murata, S. M. Zakeeruddin, M. Grätzel, R. Murdey, A. Wakamiya, *Chem. Eur. J.* **2019**, 25, 6741.
- [10] H.-A. Lin, N. Mitoma, L. Meng, Y. Segawa, A. Wakamiya, K. Itami, *Mater. Chem. Front.* **2018**, 2, 275.
- [11] F. Yang, H. E. Lim, F. Wang, M. Ozaki, A. Shimazaki, J. Liu, N. Baizura Mohamed, K. Shinokita, Y. Miyauchi, A. Wakamiya, Y. Murata, K. Matsuda, *Adv. Mater. Interfaces* **2018**, 5, 1701256.
- [12] F. Wang, M. Endo, S. Mouri, Y. Miyauchi, Y. Ohno, A. Wakamiya, Y. Murata and K. Matsuda, *Nanoscale* **2016**, 8, 11882.
- [13] F. Wang, A. Shimazaki, F. Yang, K. Kanahashi, K. Matsuki, Y. Miyauchi, T. Takenobu, A. Wakamiya, Y. Murata, K. Matsuda, *J. Phys. Chem. C* **2017**, 121, 1562.
- [14] T. Nakamura, N. Shioya, T. Shimoaka, R. Nishikubo, T. Hasegawa, A. Saeki, Y. Murata, R. Murdey, A. Wakamiya, *Chem. Mater.* **2019**, 31, 1729.
- [15] H. Nishimura, I. Okada, T. Tanabe, T. Nakamura, R. Murdey, A. Wakamiya, *ACS Appl. Mater. Interfaces* **2020**, 12, 32994.