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擬ハロゲン化物機能性誘導体を用いた高効率・安定な Sn ペロブスカイト太陽電池の開発

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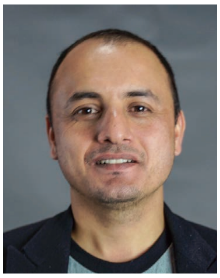

Development of High-Efficiency and Stable Sn-Perovskite Solar Cells Using Pseudohalide Functional Derivatives

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Sn ペロブスカイト系太陽電池（Sn-PSC）の提案に至るまで、私たちは Sn および Bi 系ハライドペロブスカイト太陽電池を研究してきました。Sn-PSC では、4-フルオロベンゾヒドラジドなどの多機能分子を用いた分子表面処理を施した WB-Sn ペロブスカイト（Eg〜1.68 eV）太陽電池が 11.14％のデバイス効率を達成しました。この研究は、化学工学によって欠陥化学を制御することで、効率的で安定した WB-Sn-PSC を開発する道を開くものです。

通常のバンドギャップ（Eg〜1.40 eV）の Sn-PSC では、フラーレン系多機能分子（F-COOH、F-OH、F-OSO3H）を添加剤として用いることで、Sn2＋イオンと相互作用し、Sn^{4+}の形成と非発光再結合を効果的に抑制できることを示しました。 F-COOH 添加剤を使用したデバイスでは、デバイス効率が 8.20％から 11.22％に向上し、再現性と安定性も向上しました。

Leading to our proposal on Sn-perovskite-based solar cells（Sn-PSCs）, we have explored wide/regular bandgap（WB/RB）- Sn-perovskite solar cells. For Sn-PSCs, WB-Sn-perovskite（E_g〜1.68 eV） solar cells with molecular surface treatment using multifunctional molecules such as 4-Fluoro-benzohydrazide achieved a device efficiency of 11.14％. For RB（E_g〜1.40 eV） Sn-PSCs, we demonstrated fullerene-based multifunctional molecules（F-COOH, F-OH, F-OSO$_3$H） effectively suppressing Sn^{4+} formation and non-radiative recombination. The device with the F-COOH additive exhibits an increased device efficiency from 8.20 to 11.22％, along with improved reproducibility and stability.

（1） Research content

To address the toxicity issue, there have been several attempts to replace Pb with Sn or Bi. Although Sn-perovskites（Sn-HP） are the most promising candidate, being a close cousin of Pb-halide perovskite, this class of material suffers from the facile oxidation of Sn and deteriorates the optoelectronic properties.

A. Sn-perovskite（1.68 eV） Solar cells:

Pb-free alternatives, such as Sn- and Bi-based HP materials, are projected as suitable alternatives to resolve the toxicity issue（Khadka et al. *Solar RRL* **2023**, *7*, 2300535）. Recent reports show Sn-PSCs achieving efficiencies of over 15％.（Chen et al. *Nat Photonics* 2024, *18*, 464）. But they typically have band gaps of 1.3–1.4 eV, which do not fall within the optimal bandgap range for top cells.

Therefore, WB-Sn-HPs ($E_g>1.6$ eV) are needed for Pb-free Si/perovskite tandem applications.

In this report, we demonstrated the fabrication of a WB-Sn-PSC with tin perovskite ($E_g\sim1.68$ eV), followed by molecular surface passivation using multifunctional molecules 4-Fluoro-benzohydrazide (F-BHZ).

I. Device Fabrication Method:

For the fabrication of WB-Sn-PSC, the precursors were prepared by dissolving halide derivatives and functional additive, FABr, MABr, PEABr, SnI_2, and SnF_2 in mixture of DMSO and DMF solvent. As depicted in the schematic of device fabrication (Fig. 1), we prepared inverted WB-Sn-PSCs with PEDOT: PSS (HTL), interfacial passivation layer (IPL)-F-BHZ, ICBA (ETL) by spin coating, BCP (ESL) and Ag deposited by thermal evaporation. Khadka et al. (*Small, 21, 2410048, 2025*).

II. Results and Summary:

The films with F-BHZ -IPL treatment exhibit a significant improvement in film coverage by suppressing the pinhole densities (Fig. 2a-c). We observed highly oriented crystallographic planes of (100) and (200) for Sn-HP films with IPL passivation (Fig. 2d, e). The PL intensity (Fig. 2f) is significantly increased for the ST film, suggesting the mitigation of bulk defects. The PL peaks are centered at 1.66 eV for the control and 1.68 eV for the IPL treated film corresponding to their band gap edge with blue shifting. This results in an enhancement in the device efficiency of 7.96% for control to 11.14% for IPL treated (Fig. 3a) with higher reproducibility and superior stability (Fig. 3b). The carrier transport engineering of WB-PSCs (Fig. 3c) showed better efficiency with ICBA compared to PCBM (Fig. 3d).

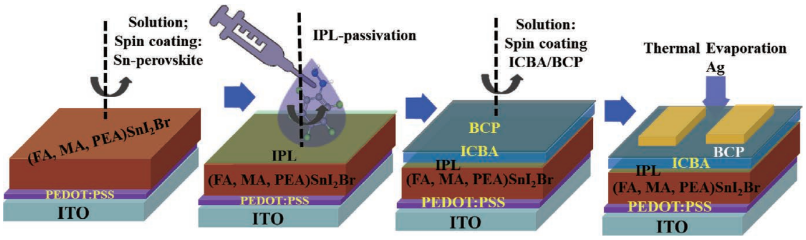

Fig. 1. Schematics of fabrication of WB-Sn-PSCs.

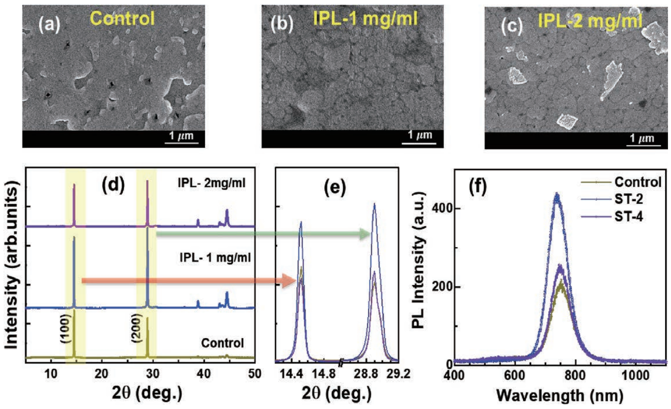

Fig. 2. SEM images of WB-Sn-HP film with varying IPL treatment of F-BHZ (a-c). XRD patterns (d,e). PL spectra (f).

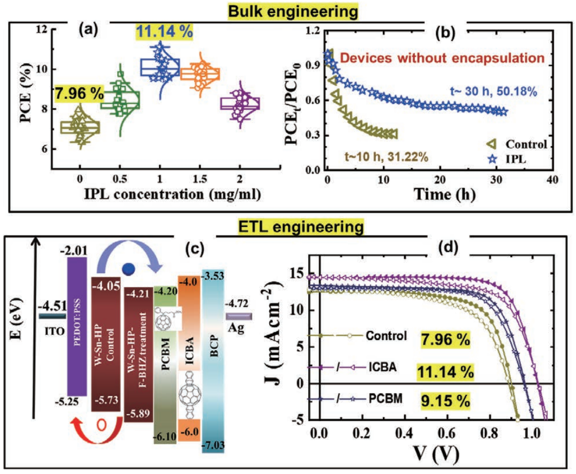

Fig. 3. Effect of IPL concentration in device efficiency (a). device stability (b). ETL engineering (c). J-V curves with ETLs (d)

B. Regular gap-Sn-perovskite (1.4 eV) Solar cells:

The functional additive technique has emerged as a critical approach to enhancing the performance and stability of Sn-PSCs.

We have demonstrated effect of fullerene derivatives (Fig. 4a) for passivation of defect and control of extent of Sn^{2+} oxidation in RB-Sn-PSCs. (*D. B. Khadka,* and co-worker J. Mater. Chem. A, 2025, DOI: 10.1039/D4TA08566C*)

I. Device Fabrication Method:

We fabricated the Sn-HP ($FA_{0.80}MA_{0.05}PEA_{0.15}SnI_3$) films with fullerene-based functional molecules as additives.

II. Results and Summary:

Fig. 4a presents ESP mapping, where F-COOH shows strong negative potential near the –COOH group, enabling effective binding with undercoordinated Sn^{2+} sites. In contrast, F-OH and F-OSO3H show weaker negative regions, indicating less effective passivation. Fig. 4b outlines the core idea that the bulky fullerene and its functional groups interact with Sn^{2+} in the $[SnX_6]^{4-}$ octahedra, potentially limiting its oxidation to Sn^{4+}. Fig. 4c highlights dominant XRD peaks for the (100) and (200) planes, indicating an orthorhombic structure. Fig. 4d shows only slight changes in absorbance near the ~892 nm band edge.

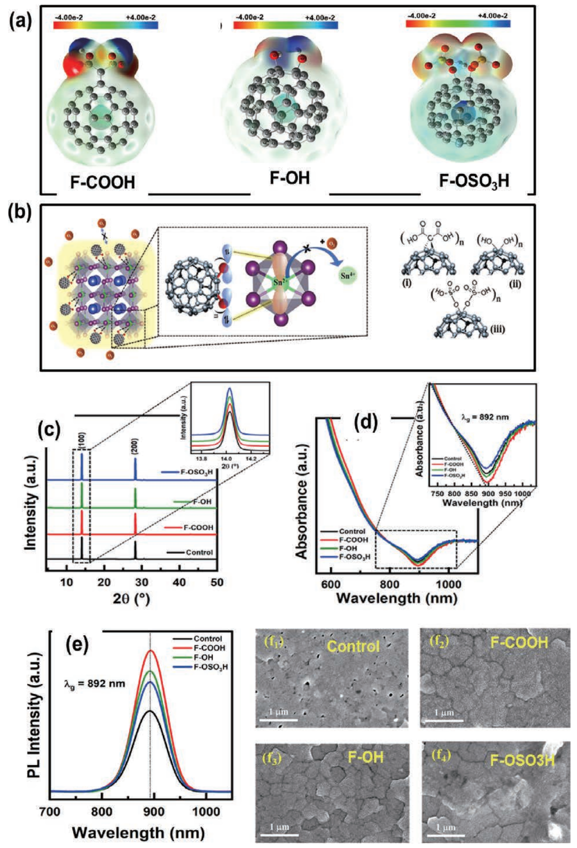

Fig. 4. Electrostatic surface potential of F-COOH, F-OH, F-OSO$_3$H (a). Schematic interaction of fullerene derivatives (b). XRD patterns (c). Absorption spectra (d). PL spectra (e). Film morphology of Sn-perovskite (f$_1$-f$_5$).

The PL spectra (Fig. 4e) show no shift in the main peak at ~892 nm (~1.395 eV), indicating it aligns with the band edge. Changes in PL intensity suggest that additives influence defect passivation in the Sn-HP film.

SEM images (Fig. 4f2–f4) reveal that additives like F-COOH, F-OH, and F-OSO3H notably enhance surface coverage and film uniformity.

Fig. 5a, b shows the cross-sectional SEM images of Sn-PSCs without and with fullerene derivative additive.

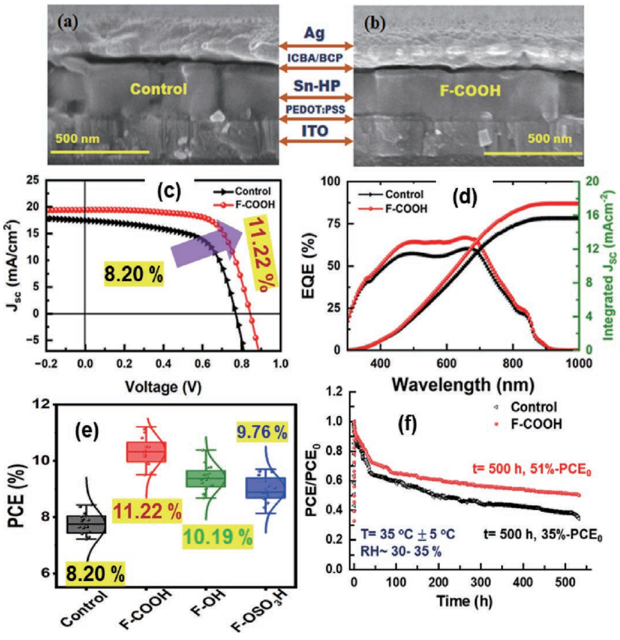

Fig. 5. Cross-sectional SEM images of RB-Sn-PSCs (a) control and (b) with F-COOH additive. J–V curves (c) and EQE (d) of devices. Statistical device efficiencies (e). Operational stability of RB-Sn-PSCs under MPPT conditions (f).

Figs. 4c, d show the current density-voltage (*J*–*V*) curves and External quantum efficiency data of the best PSCs; control (8.20%) and F-COOH (11.22%) additives. Fig. 5e demonstrates device efficiency statistics with different fullerene derivatives. In Fig. 5f, the control device's efficiency dropped to 35% after 500 hours, showing it degrades easily, likely due to moisture, oxygen, or material instability. In contrast, the F-COOH additive improved stability, maintaining over 51% efficiency, demonstrating its protective effect in perovskite solar cells.

(2) Research Achievements

"Research Paper"

1. Dhruba B. Khadka,* Y. Shirai, R. Sahara, M. Yanagida, K. Miyano, Ameliorating Defects in Wide Bandgap Tin Perovskite Solar Cells Using Fluorinated Solvent and Hydrazide. *Small*, 21, 2410048 (**2025**)
2. Dhruba B. Khadka,* Yan-Chen Kuo, Yi Zhen Li, Muhammad Waqas, You-Jia Xu, Masatoshi Yanagida, Hiroshi Nishihara, Kazuhito Tsukagoshi, Mitch M. C. Chou, Yasuhiro Shirai, and Ying-Chiao Wang, Coordination Nanosheets Stabilizing Efficient Tin-Based Perovskite Solar Cells, *ACS Appl. Mater. Interfaces 17* (18), 26813 (**2025**)
3. A. Shukla, D. B. Khadka,* C. Li, M. Rikukawa, Y. Takeoka, R. Sahara, M. Yanagida and Y. Shirai, Defect mitigation via fullerene-based functional additives for enhanced efficiency and stability in tin perovskite solar cells, J. Mater. Chem. A, 2025, DOI: 10.1039/D4TA08566C (**2025**)
4. S. Fatima, Dhruba B. Khadka,* M. Yanagida, S. K. Singh, and Y. Shirai, Effect of Alkali-Metal Additive on Rudorffite $AgBiI_4$-Based Pb-Free Solar Cells, ACS Applied Energy Materials, 8, 4601 (**2025**)
5. Dhruba B. Khadka,* M. Yanagida, Y. Shirai, Assessing degradation in perovskite solar cells via thermal hysteresis of photocurrent and device simulation, Solar Energy Materials and Solar Cells. 281, 113319 (**2025**)

"Conference Presentation"

1. D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, Molecular Passivation of Wide Bandgap Tin Perovskite Solar Cells Using Fluorinated Solvent and Multifunctional Hydrazide Derivative, MRS Spring-2025, 7th - 11th April, Contributed talk, (**USA, 2025**)
2. D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, Effect of Bifunctional Molecular Passivator for Modulating Efficiency and Stability of Inverted Perovskite Solar Cells, Asia-Pacific International Conference on Perovskite, Organic Photovoltaics, and Optoelectronics, Tokyo, Japan, (IPEROP24), 21st-23rd-17th, January, contributed talk (**Japan, 2024**)