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研究課題名（和文）Developing novel p-type BiOX oxyhalides thin layer for stable and efficient CsPbI3 perovskite solar cells

研究課題名（英文）Developing novel p-type BiOX oxyhalides thin layer for stable and efficient CsPbI3 perovskite solar cells

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研究成果の概要（和文）：このプロジェクトは、効率的で安定したCsPbX3ペロブスカイト太陽電池（PSC）の開発を目指しており、以下の結果が得られました。
アモルファスSnOxとドーパントフリーポリマーPDTDTの電荷輸送材料を開発しました。これにより、CsPbX3 PSCの高効率、特に高電圧、および優れた安定性が実現されました。CsPbX3欠陥（配位不足のPb2+と金属Pb）は、分子表面パッシベーション法によって抑制され、電圧を理論限界の92%以上に高めました。これらの研究は、電圧を上げることによってCsPbX3 PSCの低効率の問題を解決しました。安定性も、PDTDTを使用することで改善されました。

研究成果の学術的意義や社会的意義
この研究は、CsPbX3太陽電池の電圧損失と不安定性の問題を解決しました。 その結果、タンデム太陽電池や屋内太陽光発電への応用がより有望になります。
トップセルとしてCsPbX3を使用すると、タンデム太陽電池で2 Vを超える高電圧と30%を超える効率が達成され、Siパネルよりも効率的な太陽電池を提供できます。 十分な電力と駆動電圧を提供するCsPbX3屋内太陽電池を使用することで、セルフパワーのIoTシステムを実現できます。

研究成果の概要（英文）：CsPbX3 (X=I, Br) perovskite solar cells (PSCs) have potential applications in tandem solar cells and indoor photovoltaics. While the low efficiency and poor stability are limiting their perspectives. This project is aiming at developing efficient and stable CsPbX3 PSCs and the following results were achieved.
Firstly, charge transport materials of amorphous SnOx and dopant-free polymer PDTDT were developed, by which the high efficiency especially the high voltage, and good stability of CsPbX3 PSCs were realized. These materials can be used in other research on CsPbX3 PSCs. Secondly, the CsPbX3 perovskite defects (undercoordinated Pb2+ and metallic Pb) were well suppressed by a molecule surface passivation method, promoting the voltage of solar cells to over 92% of the theoretical limit. In summary, these researches solved the problem of the low efficiency of CsPbX3 PSCs by increasing the voltage. The stability of CsPbX3 PSCs was also improved by using the dopant-free PDTDT.

研究分野：ペロブスカイト太陽電池

キーワード：ペロブスカイト太陽電池　全無機ペロブスカイト　高電圧

１．研究開始当初の背景

$CsPbX_3$ perovskite solar cells (PSCs) have application potential in tandem solar cells and indoor photovoltaics. While their low efficiency and poor stability are limiting their perspectives.

(1) The low efficiency is mainly because of the low Voc. For $CsPbX_3$ PSCs, the photocurrent is approaching the theoretical limit and the fill factor is always high in most reported cases. While the Voc is still quite low and most of the reported Voc values are only 80% of the theoretical limits, leaving big space to improve.

(2) The poor stability of $CsPbX_3$ is mainly because the perovskite phase is unstable against humidity and easily transforms into a non-perovskite phase. The dopants of widely used hole transport material (HTM), Spiro-MeOTAD, can absorb humidity and trigger the perovskite phase transition, damaging the performance of $CsPbX_3$ solar cells. Therefore, improving Voc for enhancing the device efficiency and developing dopant-free HTMs are important topics for $CsPbX_3$ solar cells.

２．研究の目的

This project aims to improve the efficiency and stability of $CsPbX_3$ PSCs.

３．研究の方法

(1) For improving the efficiency, proper charge transport materials were developed for $CsPbX_3$ and the perovskite defects were suppressed by a molecule passivation engineering.

(2) For enhancing the stability, a p-type polymer was developed and used as a dopant-free HTM to avoid the hygroscopic dopant-induced perovskite phase transition.

４．研究成果

(1) The conventional charge transport materials such as TiO_2 and Spiro-OMeTAD are suitable for hybrid perovskites while not perfect for $CsPbX_3$. The main reason is the mismatch of the energy levels between these materials and $CsPbX_3$, which will lead to large energy loss at the interface and result in low Voc and efficiency. For solving this problem, on one hand, an amorphous SnOx electron transport layer (ETL) and PDTDT polymer HTM were developed. The SnOx has a slightly higher conduction band than that of perovskite, forming an interfacial spike structure, which can efficiently prevent the electron back-transfer and electron-hole nonradiative recombination. The SnOx layer remarkably improved the Voc of CsPbI2Br solar cells to 1.42 V (Figure 1), which is much higher than ever-reported values. With enhanced Voc, an efficiency of 15.53% was obtained.

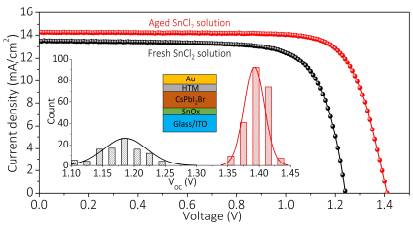

Figure 1. J-V curves of $CsPbI_2Br$ solar cells employing SnOx ETL prepared using fresh and aged $SnCl_2$ solution.

On other hand, a p-type polymer PDTDT was synthesized and used as HTM. This polymer has a proper HOMO level of -5.44 eV, which is lower than Spiro-OMeTAD and matches well with the valence band position of $CsPbI_2Br$ (-5.77 eV). It also has high hole mobility and the casted film shows a face-on orientation, both of which are beneficial for the hole transfer. When used as a dopant-free HTM, a record-high efficiency of 17.36% was achieved for $CsPbI_2Br$ solar cells (Figure 2).

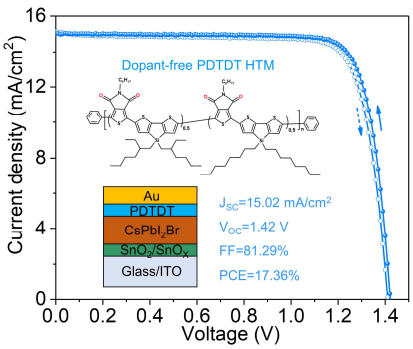

Figure 2. J-V curve of $CsPbI_2Br$ solar cells employing PDTDT as HTM.

(2) As a type of solution-processed material, perovskite film always has various kinds of defects that are bad for the device's performance. Compared with bulk defects, the perovskite surface defect property is more decisive to the performance. In this part, the surface defect property of $CsPbX_3$ was studied using density functional theory calculations and iodine vacancy was found to be the main type of defect. For reducing the iodine vacancy, i.e., undercoordinated Pb^{2+}, a thiophene-based molecule was used for surface passivation. It was found that the thiophene unit has strong interaction with Pb^{2+}, which well suppressed the iodine vacancies and the metallic Pb defects. As a result, the Voc of $CsPbI_{2.25}Br_{0.75}$ solar cells was improved from 1.36 to 1.42 V, leading to the efficiency enhancement from 15.55 to 16.72%. The Voc of 1.42 V is reaching 92% of the theoretical limit of a 1.86 eV $CsPbI_{2.25}Br_{0.75}$ perovskite, which is higher than those in reported $CsPbX_3$ solar cells (Figure 3). This method also improved the Voc of other compositional CsPbX3 solar cells, such as from 1.42 to 1.51 V (90% of limit) for $CsPbI_{1.5}Br_{1.5}$ (1.99 eV) and from 1.44 to 1.54 V (87% of limit) for $CsPbIBr_2$ (2.10 eV) solar cells, implying its universality.

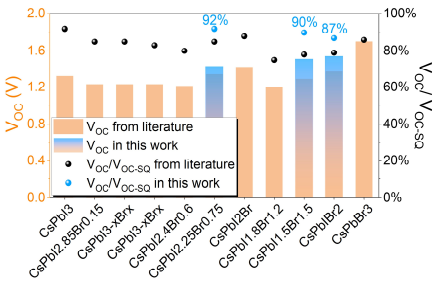

Figure 3. Summary of Voc and its ratio to S-Q limit for $CsPbX_3$ solar cells reported in literature and achieved this work.

(3) $CsPbX_3$ perovskites have an issue of poor phase stability because their perovskite phase can easily transform to a non-perovskite phase when exposed to humidity. While the widely used Spiro-OMeTAD HTM can only work efficiently with the help of hygroscopic dopants. These dopants easily absorb the moisture and trigger the perovskite phase transition, which will degrade the perovskite material stability and the device's performance. For solving this problem, the developed PDTDT polymer was used as dopant-free HTM. Except for the record-high efficiency of 17.36% achieved using this polymer (Figure 2), its effect on the stability of $CsPbI_2Br$ was studied. It was found that while Spiro-OMeTAD degraded the perovskite phase in a short time, the PDTDT-based device showed good long-term stability. The PDTDT-based samples were stored in an environment with 10-20% humidity and measured efficiency in a 20% humidity condition. After 45 days, the samples still keep 88% of the champion values (Figure 4), indicating the positive role of PDTDT in maintaining the perovskite phase and the device performance.

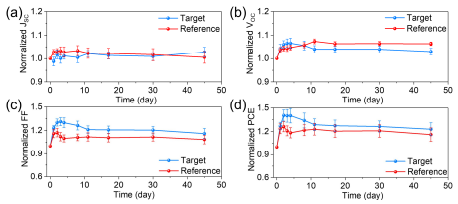

Figure 4. Long-term stability of $CsPbI_2Br$ solar cells employing PDTDT (target) and P3HT (reference) as HTM.

In summary, in this project, the efficiency of $CsPbX_3$ solar cells was improved by remarkably enhancing the Voc through the engineering of developing suitable charger transport materials and perovskite surface passivation. The stability of $CsPbX_3$ solar cells was improved by employing dopant-free polymer to replace the conventional HTM of Spiro-OMeTAD (with dopants) for avoiding the perovskite phase transition.

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５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　0件／うちオープンアクセス　0件）

１．著者名 Guo Zhanglin、Jena Ajay Kumar、Takei Izuru、Ikegami Masashi、Ishii Ayumi、Numata Youhei、Shibayama Naoyuki、Miyasaka Tsutomu	４．巻 31
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３．雑誌名 Advanced Functional Materials	６．最初と最後の頁 2103614
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adfm.202103614	査読の有無 有
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１．著者名 Guo Zhanglin、Jena Ajay Kumar、Takei Izuru、Kim Gyu Min、Kamarudin Muhammad Akmal、Sanehira Yoshitaka、Ishii Ayumi、Numata Youhei、Hayase Shuzi、Miyasaka Tsutomu	４．巻 142
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.0c02227	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

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２．出版社 Wiley-VCH	５．総ページ数 48
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〔出願〕　計1件

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〔取得〕　計0件

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関