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Photo-, Thermal-decomposition in Methylammonium Halide Lead Perovskites and inferred design principles to increase photovoltaic device stability

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Keywords

Perovskite Solar Cells; Stability; Photodecomposition; Encapsulation; Methylammonium Lead Iodide; Lead Iodide

Abstract

Published on 23 April 2018. Downloaded by University of New England on 24/04/2018 01:03:58

Hybrid lead halide perovskites have emerged as promising active materials for photovoltaic cells. Despite superb efficiencies achieved, it has been widely recognized that long-term stability is a key challenge intimately determining the future development of perovskite based photovoltaic technology. Here, we present reversible and irreversible photodecomposition reactions in methylammonium lead iodide (MAPbI₃). Simulated sunlight irradiation and temperature (40 ~ 80° C) corresponding to solar cell working conditions lead to three degradation pathways, (1) $CH_3NH_2 + HI$ (identified as the reversible path), (2) $NH_3 + CH_3I$ (irreversible or detrimental path), and (3) a reversible $Pb(0) + I_2(g)$ photodecomposition reaction. If only reversible reactions (1) and (3) take place and reaction (2) can be avoided, encapsulated MAPbI₃ could be regenerated during the off-illumination timeframe. Therefore, to further improve operational stability in hybrid perovskite solar cells, photo-, thermaldegradation processes have to be mitigated with detailed understanding. First, the device encapsulation is necessary not only to avoid contact of perovskite with ambient air, but also to prevent leakage of volatile products released from perovskite. Second, a careful selection of organic cations in the perovskite compositional formula is needed to avoid any irreversible reaction. Third, selective contacts must be as chemically inert as possible against volatile released products. Finally, hybrid halide perovskite material is assumed to undergo a dynamic of formation and decomposition process and this could gradually decrease perovskite's crystalline grain size with time. Therefore, efforts on depositing highly and large crystalline perovskites could be efforts in vain in regards to the long-term stability.

Introduction

Hybrid lead halide perovskites have been intensively evaluated as light harvesting materials for photovoltaic cells since 2009.¹ Currently, long-term stability of perovskite solar cells is one of the major challenges where substantial efforts are needed to move forward hybrid perovskite solar cells towards commercialization.² Meanwhile, a significant number of research groups are achieving power conversion efficiencies over 20% using hybrid perovskite devices,³ very few devices have succeeded in operational stability tests showing lifetimes longer than 1000 hours

at the maximum power point.³ Although promising attempts have been realized recently to improve durability of these cells by using different approaches as chemical inert scaffolds and electrodes,⁴ or mixed/multication hybrid perovskites.⁵ How hybrid perovskite suffers from degradation and what products are generated during the degradation are important questions to be answered in order to design stable perovskite-based solar cells. Furthermore, understanding of reversible degradation routes or the so-called self-healing in perovskite solar cells, which the cell performance recovers to the original value after resting in dark, has recently received attention as a strategy to prolong lifetime.⁶ In the decomposition pathways of methylammonium based perovskites the must-avoided degradation processes are irreversible degradation reactions limiting life time of the solar cells permanently. Therefore, the understanding of fundamental processes taking place in both reversible and irreversible degradation pathways is a step forward to advance in enhancing the stability of solar cells. Our group recently found that MAPbI₃ perovskite degrades significantly faster upon exposure to I_2 vapor than H_2O , O_2 , or light only.⁷ As highlighted by Wilks and Bär,⁸ we proposed that the internally generated I₂ and its migration within MAPbI₃ induced by solar cell operation and/or external stimuli (such as H2O, O2, light irradiation, applied bias, and heat) leads to a selfsustaining and irreversible degradation reaction in perovskites independent of device architecture.⁷ Additionally, we recently showed that CH₃I and NH₃ are generated as irreversible gas by-products during high temperature thermal degradation of $MAPbI_{3}$. However, the condition in which detrimental I_2 is generated remains unclear.

Interestingly, this missing puzzle is associated to a work published by Dawood *et al.* in half a century ago regarding lead iodide (PbI₂).¹⁰ PbI₂ is a relevant material in the topic of perovskite solar cells. For example, PbI₂ is a regular reagent choice to synthesize hybrid perovskite and also it is the unique remaining degradation solid product after degradation of MAPbI₃. Dawood

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et al. found that PbI_2 suffers photodecomposition to iodine gas (I₂) and lead (Pb⁰) upon interaction with visible light by observing electrical conductivity drop under illumination wavelengths above PbI_2 band gap.¹⁰ They, then, suggested the following stepwise PbI_2 photodecomposition route: (I) photodecomposition of PbI_2 takes place assisted by two excitons generation mechanism (two electron-hole pairs); (II) these two excitons react, leading to formation of a Pb⁰ atom, and (III) formation and release of I₂ molecule leaving two positive charged anion vacancies sites (V₁⁻),¹¹ see Figure 1a.

By reexamining Dawood *et al.*'s work, here we present the following two points: (1) systematical investigation of light-only decomposition pathways of PbI₂ by checking that our experimental setup (Figure1b) is able to detect I₂ release and then to pursue gas release detection on MAPbI₃ and (2) photodecomposition experiments on MAPbBr₃ aiming to shed light on "*why MAPbBr₃ stability is higher than MAPbI₃ perovskite?*"

Our experiments were performed in a home-built small vacuum chamber in the absence of H₂O and O₂ eliminating all other possible external degradation factors. Inside this vacuum chamber, applied light and/or heat and measured temperatures were accomplished *in situ* directly on the sample holder, and the released gaseous species during photodecomposition were probed using a quadrupole mass spectrometer (MS) equipped with an electron multiplier detector. Based on this setup, light induced activation energies for I₂ release from PbI₂ and MAPbI₃ were extracted and compared. Thin-films of PbI₂, MAPbI₃ and MAPbBr₃ materials before and after photodecomposition procedure were studied by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to identify the remaining non-volatile degraded solid products. Finally, we also investigated whether photodegraded PbI₂ films containing Pb⁰ could be recovered to PbI₂ by exposing to I₂ pellets at room temperature, which showed the reversibility

of this photodecomposition. We propose that hybrid lead halide perovskite materials under mild visible illumination and temperature conditions is reversible; *i.e.*, a continuously decomposing and re-forming dynamical process takes place, which establishes a chemical equilibrium between gas phase components and solid perovskite.

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Figure 1 | Schematic illustration of photodecomposition, thermal evaporation and thermal degradation processes in PbI_2 and $MAPbI_3$. a) (0k0) plane view of layered PbI_2 supercell. The figure depicts the two steps for the release of I_2 and generation of Pb⁰ by the two-exciton mechanism. b) Schematic drawing of the experimental setup for controlled PbI_2 and perovskite degradation experiments. H: electrical heater, T: thermocouple, P: crystal/cold cathode pressure gauge, MS: quadrupole mass spectrometer, top quartz window and Xe lamp or LED light sources with controlled on/off intervals. c) PbI₂ decomposition process driven by visible light (< 530 nm) above PbI₂ band gap at 40-60 °C, d) Temperature assisted PbI₂ evaporation at ~ 70 °C in dark, and e) MAPbI₃ photodecomposition and thermal degradation processes leading to irreversible decomposition to organic volatile gas species ($CH_3I + NH_3$), reversible decomposition (CH₃NH₂ + HI), and reversible generation of I₂ and non-volatile Pb⁰ under illumination or mild heat conditions. Irreversibility of the process releasing $CH_3I + NH_3$ is indicated by one-directed arrow for the reaction. Crystal phases database used for depicting the structures were ICSD-68819 for PbI₂, ICSD-96501 for the cubic Fm-3m Pb⁰ phase and ICSD-238610 for tetragonal MAPbI₃. Correlated partial occupation for methylammonium cation in MAPbI₃ phase was solved using Supercell.¹

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Results and discussion

PbI2 degradation under illumination and dark conditions.

First, we performed the photodecomposition experiments on PbI_2 (Figure 1c) in our homedesigned experimental setup (Figure 1b) to verify the adequacy of this setup for I_2 detection prior to compare with photodecomposition on MAPbI₃. Two important findings by Dawood et $al.^{10}$ were: (1) I₂ gas and metallic Pb⁰ generations as a consequence of PbI₂ photodegradation with activation energy (E_a) of 4.7 kcal/mol, and (2) a threshold wavelength of 520 nm, where only higher photon energies initiate the photodecomposition of PbI₂. These findings were also observed in our set-up free moisture and anaerobic regimes but detecting I_2 gas release at temperatures as low as 40-60 °C. We probed four different pulsed light sources, three LED light sources: red (617 nm), blue (470 nm), white (450 + 550 nm) and Xe lamp based simulated solar irradiation (0.55 Sun). Also, an experiment at dark conditions but heating the sample stage at similar temperature level as during lightning experiments was carried out to decouple photodecomposition and thermal degradation (or evaporation) processes (Figure 1d). Details of experimental procedures are found in Methods section and Supplementary Information file. Next, experimental E_a for the I₂ release during PbI₂ photodecomposition process was extracted in order to determine the feasibility of this photodecomposition reaction. In our analysis, the corresponding I_2 release using different light sources were estimated from MS data trace pulses, see Table 1.

Table 1. Estimated* activation energies (E_a, kcal/mol) corresponding to I₂ release reaction (eq.

 1).

	Wavelength (nm)	Temperature	Light Intensity	Ea
Light Source		(°C)	(mW/cm ²)	(kcal/mol)
White LED	450 + 550	50-70	80-110	57
Blue LED	470	45-62	71-120	45
Xe lamp	~ Sun	35-78	55	9

*Details on E_a determination and wavelength spectra distribution for each light source are shown in Supplementary Sections S4 and S5, respectively.

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 E_a showed strong dependence in magnitude and wavelength distribution of light source employed. The simulated sun light (Xe lamp, Table 1), which has a broader spectral wavelength lead to the smallest $E_a \sim 9$ kcal/mol compared to narrow wavelength interval generated by LEDs ($E_a \sim 45$ k/cal and 57 kcal/mol for blue and white LEDs, respectively). Interestingly, despite the different photodegradation conditions employed in the current study (*i.e.*, high vacuum and absence of O₂), the extracted E_a corresponding to PbI₂ degradation under Xe lamp illumination (55.2 mW/cm²) agrees well with the E_a value reported by Dawood *et al.* (4.7 kcal/mol).¹⁰

Further investigations using XRD and XPS techniques revealed that Pb^0 was the remaining non-volatile products from the photodecomposition of PbI_2 . More interestingly, this decomposed Pb^0 product showed also a reversible recovery process back to PbI_2 after shorttime exposure to I_2 gas (Supplementary Section S7-S8).

In summary, the chemical and physical processes extracted from all the sets of degradation and recovery experiments on PbI₂ powders and thin-films are summarized by Equation 1 as well as illustrated in Figure 1c. Under illumination with photon energies higher than 2.34 eV (< 530 nm), photodecomposition takes place but it is a reversible process if Pb⁰ is exposed again to I₂(g),

$$PbI_2(s) \xrightarrow{h\nu} Pb^0(s) + I_2(g)$$
 (1)

haa

Under dark condition at moderate temperatures (~70 $^{\circ}$ C) in high vacuum (~10⁻⁶ Torr), PbI₂ sublimates in the form of molecules or clusters as depicted in Figure 1b or described in Equation 2 below,

$$PbI_2(s) \xrightarrow{a} n PbI_2(g)$$
 (2)

Noteworthy, no traces of released I2 gas were observed during dark and mild temperature conditions.

MAPbI₃ and MAPbBr₃ degradation under illumination and dark conditions.

In the previous section, PbI_2 photodecomposition and its volatile (I₂) and non-volatile (Pb^0) decomposition products as well as recovery routes were established based on our home-built setup. Identical experimental conditions were applied to MAPbI₃ perovskite. In addition, we also studied the photodecomposition of MAPbBr₃ for comparison purposes as this material has been reported to show higher stability than MAPbI₃.^{7, 13, 14} Currently, the origin of this

difference remains largely elusive and such relative stability has also found contradictory results.¹⁵

MAPbI₃ was introduced in the vacuum chamber and after pumping down the system ($\sim 10^{-6}$ Torr), a set of Xe lamp illumination light pulses and only heating pulses under dark condition experiments were carried out. Sample temperature and MS traces recorded are displayed in Figure 2a,b for each experiment. Firstly, it was striking to note that the hybrid perovskites required much longer time (\sim 72 h) to reach a similar level of high vacuum condition compared to PbI₂ (~6 h). MS data helped to clarify the reason of this phenomenon. One of the most important findings from this experiment is that in contrast with PbI₂, MAPbI₃ powder sample releases I_2 independently of light or dark conditions. The rate of I_2 generation was relatively constant during the light/dark pulse conditions (Figure 2a), whereas I₂ was only generated at high temperature pulses (> ~60 °C) applied during heat-in-dark condition (Figure 2b). Under mild temperature conditions (< ~60 °C), I₂ release is minimized. This indicates that MAPbI₃ continues to degrade for a while once it is exposed to the light source. Unlike PbI₂, MAPbI₃ does not have a threshold in wavelength where I2 is released by photodecomposition. If this threshold exists because the band gap on MAPbI₃, an infrared light source should be used and therefore we prefer to use directly heating the sample in dark conditions. Furthermore, in addition to I₂ release, MAPbI₃ perovskite was continuously releasing the organic gas components (CH₃NH₂, HI, CH₃I and NH₃) under vacuum conditions. Upon MAPbI₃ insertion into the vacuum chamber, the background signals associated to MAPbI₃ degradation detected by MS were observed to increase. Such an increase was further enhanced during the pulse rises of light or temperature. Furthermore, mass peaks corresponding to dimethylformamide (DMF) solvent can be observed.¹⁶ Such occluded solvent molecules in the perovskite were expected to be detected because perovskite powder samples were prepared by using a protocol similar to

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the typical spin coating deposition method, see Methods and Supplementary Section 1. E_a values for the I₂ release in MAPbI₃ were extracted to compare with the PbI₂ case, see Table 2.



Figure 2 | Mass spectrometry profiles of MAPbI₃ and MAPbBr₃ decomposition products during illumination and heating-at-the-dark pulses experiments. a) Light/dark intervals (5 min each) on MAPbI₃ perovskite sample using a Xe lamp delivering 55 mW/cm² of light power. White and grey areas represent under light and dark pulse duration, respectively. The black lines correspond to the sample temperature. b) Heating on/off intervals (5 min each) on MAPbI₃ sample under dark conditions. Species of interest detected in MS are labeled in the right side. Right panel shows calibrated mass traces for c) CH₃NH₂, d) CH₃I and e) I₂ during the heating intervals in dark conditions. Supplementary Figure S14 shows calculated CH₃I/CH₃NH₂ molar ratio. f) Light/dark intervals (3 min each) on MAPbBr₃ perovskite sample. g) Heating on/off intervals (3 min each) on MAPbBr₃ using a heating rate of 20 °C·min⁻¹ under He atmosphere in a TG/DTA equipment using the same setting as recently published for MAPbI₃ perovskite.⁹ Release of CH₃Br (m/z = 94 and 96 amu traces) is observed during the thermal degradation. Supplementary Figure S13f shows the fragmentation pattern for CH₃Br molecule.

Table 2.	Estimated*	activation	energies	(kcal/mol)	for the	degradation	reactions	releasing I2	2 in
MAPbI ₃	samples as 1	measured by	y MS spe	ctrometry.					

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	Temperature	Light Intensity	
Light/dark conditions	$(^{\circ}C)$	(mW/cm^2)	E _a (kcal/mol)
Xe lamp	35-72	55	6
Heat in dark	60-84	0	18
	1 1 1		

*Details on E_a determination and wavelength spectra for each light source are shown in Supplementary Sections S4 and S5, respectively.

Interestingly, the E_a value corresponding to I_2 release in MAPbI₃ (~6 kcal/mol) was slightly lower to that in PbI₂ (~9 kcal/mol), which indicates that I_2 release in MAPbI₃ is even slightly more favorable than in PbI₂. Because I_2 release was observed in dark conditions, E_a was also calculated for MAPbI₃ from I_2 released signal during heating-in-the-dark experiments. We noticed that E_a in the heating in dark condition was around three times higher compared to that of under light exposure meaning that light-driven process is dominant in MAPbI₃ degradation phenomena.

Similarities and differences found for MAPbI₃ and PbI₂ during these light/heat stress experiments rely on two possible reasons (considering that MAPbI₃ material system is at some

extent represented by PbI₂ with intercalated MA⁺ cations): (i) in contrast to PbI₂, MAPbI₃ shows smaller band gap, suggesting that additional photons with lower energies become effective for exciton and/or free charge generation at the same illumination power, and (ii) I₂ release in MAPbI₃ does not need a two exciton mechanism as PbI₂ because [PbI₆] octahedral distortion produces shorter I-I bond distances consistent with the formation of neutral I₂ defects,¹⁷ which potentially facilitates the release of I₂.¹⁸

For the sake of completeness, the same photo-, thermal decomposition experiments performed on PbI₂ and MAPbI₃ were applied to MAPbBr₃ to elucidate its decomposition products (*e.g.*, is Br₂ generated? What organic molecules are released from degraded MAPbBr₃?) and associate it with the reported disparity in the stability of MAPbBr₃ compared to MAPbI₃. Comparing the experimental observations on photodecomposition between MAPbI₃ and MAPbBr₃ perovskites, the main difference was that under vacuum and near room temperature conditions, MAPbI₃ showed all a plethora of degradation gas products (*i.e.*, CH₃I and NH₃; CH₃NH₂ and HI; and I₂), but MAPbBr₃ only released CH₃NH₂ and HBr (and solvent), Figure 2f,g. We emphasize that CH₃Br, NH₃, and Br₂ gaseous species detection were below the signalsensitivity threshold of MS under vacuum conditions at low temperature range (30-70 °C). On the other hand, under near atmospheric inert He pressure conditions and at high temperatures (~300 °C), MAPbI₃ and MAPbBr₃ underwent similar degradation processes of releasing CH₃I/NH₃ gas products (MAPbI₃)⁹ and CH₃Br/NH₃ (MAPbBr₃) (Figure 2h), respectively. Table 3 summarizes both experimental conditions and detected products from degradation tests carried out in perovskites.

Table 3. Summary of experimentally detected volatile degradation products under differe	nt
environmental conditions. As comparison previously reported degradation products are also	so
indicated in the table.	

Perovskite type	Inert atmosphere:	Inert atmosphere:		
	Vacuum	~ 1 atm, Helium		
	T ~ room	T ~300 °C		
MAPbI ₃	1) CH ₃ NH ₂ + HI * ^{,‡}	$NH_3 + CH_3I^{\dagger}$		
	2) NH ₃ + CH ₃ I * ^{,‡,#}			
	3) I ₂ *			
MAPbBr ₃	$CH_3NH_2 + HBr *$	NH ₃ + CH ₃ Br *		

* This work. [†] Ref. no. 9. [‡] Ref. no. 19. [#] Ref. no. 20 assuming that an iodine-transfer polymerization reaction was involved on the CH₃I monomer to form radical species as CH₃CH₂[•] which can propagate to form a longer polyethylene chain as observed in the work by Ke et al.

In summary, the chemical processes extracted from all the sets of degradation and recovery experiments on halide perovskite powders and thin-films are summarized by Equation 3 and 4 as well as illustrated in Figure 1d for MAPbI₃. Under illumination or dark low heating conditions compatible with photovoltaic operation, photo-, thermal-decomposition reactions take place as,

$$MAPbI_{3}(s) \stackrel{hv \text{ or } \Delta}{\longleftrightarrow} PbI_{2}(s) + Pb^{0}(s) + I_{2}(g) + CH_{3}NH_{2}(g) + CH_{3}I(g) + HI(g) + NH_{3}(g)$$
(3)

$$MAPbBr_{3}(s) \stackrel{hv \text{ or } \Delta}{\longleftrightarrow} PbBr_{2}(s) + CH_{3}NH_{2}(g) + HBr(g)$$

$$\tag{4}$$

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The CH_3X/NH_3 (X = I or Br) molecules are reported to be the thermodynamically driven product of degradation of methylammonium cation,¹⁹ and such degradation is irreversible to form back again $MA^{+,9}$ In contrast, released $CH_3NH_2 + HX$ is considered to be reversible because of its high reactivity in neutralizing back to MA⁺ and X⁻. In fact, CH₃NH₂/HI gases have been demonstrated as excellent reagents used directly to synthesize

MAPbI₃ perovskite.^{21, 22} Therefore, under encapsulated conditions, the consideration of $CH_3NH_2 + HI$ released gases as degradation products from perovskites would not be a correct term as they are able to resynthesize MAPbI₃. A unique situation where $CH_3NH_2 + HX$ could be considered as degradation products is when perovskites are placed in an open system (*e.g.* non-encapsulated solar cells) where back reaction is obviously inhibited because the released gases are permanently leaked. As highlight from our work, we determined $CH_3NH_2 + HI$ release as a *benign* or reversible pathway of degradation in such a way that it does not lead to the permanent degradation, but to a chemical equilibrium of formation and destruction of perovskite (Figure 1e).

On the other hand, the back formation to MAX or MAPbX₃ from the released CH₃X + NH₃ molecules is thermodynamically unfavorable and prone to form non-primary ammonium salts as previously reported.⁹ Therefore, we assign the CH₃X + NH₃ release to be an authentic detrimental pathway for perovskite degradation. If such a degradation path is taking place even in smaller proportions as represented in Figure 2c,d or elsewhere,¹⁹ it would be the culprit of short time stability of methylammonium based hybrid perovskites solar cells regardless of employing a careful encapsulation. In view of above points, it can be understood that MAPbBr₃ is more stable than MAPbI₃ because this detrimental path releasing CH₃Br + NH₃ was not observed when kept at low temperatures, *i.e.*, 40-80 °C (see Table 3 and equation no. 4). Consequently, an encapsulated sample of methylammonium based bromide perovskite would be more stable than I-based perovskite under near ambient conditions.

Photo-, thermal instability of pristine perovskite: implications for their operational stability on solar cell devices.

Perovskite thin-films employed in photovoltaic devices under working conditions could follow a different degradation path compared to that of pristine polycrystalline powder samples used in this study. In fact, this study on photo-, thermal-decomposition of perovskites, the light harvester material is placed on purpose at the at the optimistic and favorable conditions for perovskite stability avoiding contacts with any other compound (e.g., HTL, ETL, dopants used in HTL, moisture or oxygen) and also without any applied bias. At this point it is important to remind that chemical synthesis procedure of pristine perovskite as well as temperature and illumination conditions during the tests can be considered similar to perovskite submitted under working conditions in devices.

In regard to selective contacts, what side reactions are going to suffer for example a specific HTL used in photovoltaic devices upon exposure to these gas by-products (HI, CH₃I, I₂, CH₃NH₂ and NH₃) released for example by MAPbI₃ during working conditions (eq. no 3), it is out of scope of this work. However, it is suggested that rarely the spiro functional group in the spiro-MeOTAD molecule, which is widely used as HTL, could resist the attack of these above chemical gas agents during ~20 years of photovoltaic device lifetime. Therefore, avoiding contact with other compounds related only to the device allows to unveil the intrinsic pathways of photo-, thermal-decomposition in perovskite. It could be reasonably considered that the selective contacts could not avoid these intrinsic decomposition paths in perovskites driven by light and temperature. Contrarily, the decomposition would become worst following unknown side reactions specific for each selective layer case.

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On the other hand, voltage applied in thin-film is a relevant parameter to take in account when measuring photo-, thermal-degradation in halide perovskites. In regard to degradation paths for perovskite under applied bias, additional experimental work is carried out in a specially designed MAPbI₃ thin-film device consisting of two-gold electrode contacts (spaced by 70 microns) deposited on MAPbI₃. Controlled bias voltage is applied on the gold electrodes

generating an electric field corresponding to that of typically being generated in perovskite solar cells ($\sim 0.71 \text{ V/}\mu\text{m}$). In this case, perovskite layer is protected from moisture and oxygen by a top CYTOP layer. The core levels of MAPbI₃ thin-films were investigated using XPS mapping on lateral devices (Figure 3). As can be seen in Figure 3a, a uniform distribution of Pb²⁺ and I⁻ belonging to MAPbI₃ was found. However, after applying the electric field (Figure 3b) a clear decrease as well as non-uniform distribution in the Pb^{2+} and I was observed. XPS spectra (Figure 3c) was also collected from the area between the electrodes (using a 27µm detector slit). A clear formation of Pb^0 and Pb^{2+} depletion was observed in the negative electrode side where reduction process takes place in the perovskite after the externally applied electric field. Similarly, a broadening of the FWHM belonging to I3d core level (from 1.0 to 1.4 eV) was observed after applying the electric field. The broadening of the I3d FWHM indicates formation of new iodine species, such as CH₃I, HI and I₂. Overall, the XPS results in this experiment are consistent with the observations described in the unbiased pristine perovskites case. However, the most impressive fact in these biased thin-film perovskite experiments is the *in situ* observation of violent release of gases observed in the form of "bubbles" formed under the CYTOP transparent layer. The CYTOP layer is effectively impeding such release of volatile gases from perovskite to the ambient. (Figure 3d and deposited video film as SI file).

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Figure 3. XPS mapping and spectra (Al- K_{α} = 1486.6 eV) of MAPbI₃ thin films before and after voltage bias. a, b) XPS maps of Au 4f_{7/2}, I 3d_{5/2}, and Pb 4f_{7/2} core levels and c) XPS spectra of Pb 4f and I 3d core levels before and after electrical bias. The FWHM of the I 3d peak is 1 eV and 1.4 eV before and after bias applied, respectively. The bias voltage applied is 50 V across 70 µm, $\varepsilon = 50/70 = 0.71V/\mum$. Under conventional cell operation at maximum power point, it would be 0.8 V across 0.5 µm of perovskite, $\varepsilon = 0.8/0.5 = 1.6 V/\mum$. The Pb⁰/Pb²⁺ composition ratio is 0.20 in biased degradation sample. It is similar to 0.18 composition ratio obtained from unbiased sample (see Table S2 and Figure S15b). The composition ratio for I 3d in biased degraded sample is 1.8. This ratio is 1.6 for the unbiased degraded sample (see Table S2 and Figure S17a). d) Video frame of illuminated device under V bias showing the release of volatile gases in the negative electrode and trapped gas bubbles under the transparent CYTOP layer. See SI file for full video of the experiment.

The challenges associated with these chemical instability issues found in MAPbI₃ perovskite must be mitigated in perovskite solar cells. Below, four guideline/recommendations based on the outputs of above degradation study could help to design better devices with increased operational stability:

(1) Careful selection of cations for the A site in perovskite structure replacing MA^+ with the proper mixture of Cs^+/FA^+ (cesium and formamidinium) cations. Irreversible reaction

(CH₃I/NH₃ formation and release route) suffered by MA⁺ can be solved in principle by replacing it using a mixture of Cs⁺/FA⁺ (cesium and formamidinium cations) in the A site of perovskite without large efficiency losses. More difficult if not impossible at the moment could be to find an atomic or molecular replacement for the iodide ion still maintaining excellent light harvesting properties.

- (2) Encapsulation of devices is necessary not only to avoid contact with external agents, but also to prevent the volatile decomposition products leakage (I₂ for all iodine based perovskites and CH₃I/NH₃/CH₃NH₂/HI for the specific MA⁺ based perovskite case). Encapsulation provides that perovskite is inside a thermodynamic closed system allowing only energy exchange and Law of Mass Action stating chemical equilibrium concentrations of solid and gas products according to perceived temperature.
- (3) Selective contacts in solar cell, especially organic molecular or polymeric based HTM, must be chosen as chemically inert as possible to be not affected by an environment rich in one of the most acidic molecules (HI), good methylation reagent (CH₃I), oxidizing agent (I₂) and mild to high base as CH₃NH₂ and weak base as NH₃.
- (4) In relation to point no. 2 above, hybrid halide perovskite material is assumed to undergo cycles of dynamic formation and decomposition process and this could gradually decrease its crystalline grain size in time. Therefore, efforts on depositing large crystalline perovskite domains could be efforts in vain in regards to the long term stability.

Conclusions

In summary, hybrid lead iodide perovskite has been demonstrated as a semiconductor material that exhibits dynamic processes of continuous decomposition and formation under visible light and/or mild temperature stimulus compatible with solar cells operation conditions. I₂ gas is released from MAPbI₃ even in dark conditions during mild heating as low as 40-80 °C, which

corresponds to solar cell working temperatures. Fortunately, this photodecomposition reaction is reversible at least for PbI₂, since back formation $Pb^0 + X_2 \rightleftharpoons PbX_2$ is observed. Because MAPbI₃ decomposes also into CH₃I + NH₃, which corresponds to the irreversible degradation pathway, strategies such as replacement of MA⁺ cations by more stable Cs/FA mixed combinations are suggested. MAPbBr₃ shows enhanced stability than MAPbI₃ because the former decomposes only into CH₃NH₂ + HBr at ambient temperature, which allows a clean self-healing process. Therefore, to further improve the operational stability in hybrid perovskite solar cells, all these photo-, thermal-degradation processes have to be controlled with detailed understanding. Four guideline/recommendations based on the outputs of above degradation study could help to design better devices with increased operational stability. First, the device encapsulation is necessary not only to avoid contact with ambient air, but also to prevent leakage of volatile released products. Second, a careful selection of organic cations in the A site for the compositional perovskite formula is needed to avoid any irreversible reaction. Third, selective contacts must be as chemically inert as possible against volatile released products which could provoke undesired side-reactions. Finally, hybrid halide perovskite material is assumed to undergo a dynamic formation and decomposition process and this could gradually decrease its crystalline grain size with time. Therefore, efforts on depositing highly and large crystalline perovskite could be efforts in vain in regards to the long term stability.

Comment from Authors

Published on 23 April 2018. Downloaded by University of New England on 24/04/2018 01:03:58

During the course of the review of this manuscript an article (https://doi.org/10.1038/s41563-018-0038-0) appeared describing the enhancement of ion conduction in perovskite by the effect of light. It is a surprising effect assumed to vacancies generation on perovskite which is better

understood based on our MS measurements during soft temperature and light conditions degradation tests.

AUTHOR CONTRIBUTIONS

Y.B.Q. conceived the idea and supervised the work. E.J.J.P. and Y.B.Q. designed the experiments. E.J.J.P. carried out all measurements (except XPS), data analysis, results interpretation, and wrote the first version of the manuscript. L.K.O., M.M. and Z.H performed XPS measurements and assisted with XPS data analysis and interpretation. E.J.J.P. recorded and edited the "bubbling" perovskite video deposited as SI file. All authors assisted with interpretation of the results and contributed to writing the manuscript.

ACKNOWLEDGMENT

This work was supported by funding from the Energy Materials and Surface Sciences Unit of the Okinawa Institute of Science and Technology Graduate University, the OIST Proof of Concept (POC) Program, the OIST R&D Cluster Research Program, and JSPS KAKENHI Grant Number 15K17925. We thank Steven D. Aird, the Technical Editor at Okinawa Institute of Science and Technology Graduate University for valuable suggestions in revising the manuscript.

Journal of Materials Chemistry A Accepted Manuscript

Methods

Materials. Lead (II) iodide (PbI₂, 99.9%) was purchased from Tokyo Chemical Industry Co., (PbBr₂, 99.999%) was purchased from Sigma-Aldrich, Ltd, lead (II)bromide methylammonium iodide (MAI) and methylammonium bromide (MABr) were purchased from Dyesol Limited. All chemicals were used as received without any further purification. Hybrid perovskites in powdered polycrystalline material form were obtained mimicking the procedure to deposit perovskite thin films on substrates. Briefly, 1 mL of DMF (Wako Pure Chemical Industries) solution (~1 M) containing desired stoichiometric precursor quantities to synthesize MAPbI₃ or MAPbBr₃ was poured on a mortar with 10 cm in diameter and kept at 100 °C inside a fume hood. Precursor solution was slowly spread on the mortar surface helped by the pestle. DMF solvent was evaporated within 1-2 minutes, which resulted in a solid crystalline material on the mortar. The crystal was then carefully collected. Perovskite phase purity (*i.e.* absence of PbI₂) and crystalline parameters were checked from powder XRD measurements (Supplementary Figure S1). Powder XRD were recorded in glazing incidence XRD (GIXRD) mode (detector scan, omega=0.5°) using D8 Bruker Discover (Cu-Ka1 radiation) with 20 degrees varying from 10° to 55° using 0.5 s of acquisition time for every 0.02° 2 θ intervals. Quantitative analysis of powder samples were obtained by fitting the entire XRD pattern with MAUD 2.71 software package.²³

Photodecomposition experiments. (i) Probing of volatile gases. Fresh samples of PbI_2 (~180 mg) were loaded in the sample holder located inside the chamber (Supplementary Figure S2a). Upon reaching high vacuum level (~10⁻⁸ to 10⁻⁶ Torr) monitored by a pressure gauge, MS spectrometer was switched on. The temperature of the sample under dark conditions and high vacuum conditions were slightly high (30-35 °C) due to the e-ionization (radiative heating) of

View Article Online DOI: 10.1039/C8TA03501F

MS. Light power pulses of white, red, and blue LEDs were programmed using Autolab PGSTAT204 potentiostat including the LED driver box accessory (Metrohm AG). Simulated sun-light was generated using a 150 W short-arc Xe lamp from the Portable Solar Simulator (PEC-L01, Peccell Technologies Inc). Light pulses in the solar simulator were computer controlled remotely by a homemade program and actuator. Light power delivered by both solar simulator and LEDs were calibrated using a calibrated silicon photodiode accounting quartz window and distance from light source to sample holder (Supplementary Section S5 for light power calibration details). Volatile degradation traces were recorded using a quadrupole MS equipped with an electron multiplier detector (SRS Stanford Research Systems, RGA300). Conventional Faraday cup detector in MS was not reliable to detect diiodine traces at nearly room temperature. MS raw signals were calibrated using sensitivity factors calculated following the procedure described in Supplementary Section S6. (ii) Probing of non-volatile **products.** The chemical composition determination of non-volatile products (*i.e.* remaining solid material) from the photodecomposition experiments were performed by XRD and XPS (Supplementary Section S7). The surfaces chemical properties of PbI₂, MAPbI₃ and MAPbBr₃ were characterized by XPS (Kratos AXIS ULTRA HAS, monochromated Al-K α = 1486.6 eV) in order to observe the effect of light exposure in vacuum. The binding energy (BE) was calibrated by measuring the Fermi edge ($E_F = 0 \text{ eV}$) and Au-4f_{7/2} (84.0 eV) on a clean Au surface. Freshly prepared samples were first analyzed by XPS. The BE scale of PbI_2 spectra was calibrated using the adventitious carbon peak (C 1s) at ~285 eV as reference.^{24,25} In our samples, residual amounts of adventitious carbon would be unavoidable due to air exposure prior to the XPS measurements. In addition, C 1s signal originating from residual solvents may be also expected. Great care was taken in order to minimize X-ray exposure time when acquiring XPS signal on PbI₂, MAPbI₃, and MAPbBr₃ samples. X-ray-induced sample damage

was monitored by taking five consecutive scans and comparing these spectra. Acquisition time for each scan varied from 20 to 70 s depending on the core level regions. The five scans were averaged to a single spectrum if no significant change was observed. Peak fittings and standard deviation calculations were performed with CasaXPS 2.3.16. Shirley function was used to simulate the background signal due to inelastic scattering processes.²⁶ Raw XPS spectra of Pb 4f, I 3d (for PbI₂ and MAPbI₃), Br 3d (for MAPbBr₃), C 1s, and N 1s (for MAPbI₃ and MAPbBr₃) were fitted with Gaussian-Lorentzian (G-L) functions to quantitatively determine BE peak positions, full width at half maximum (FWHM), and the relative spectral areas. The intensity ratios between the $4f_{7/2}$ and $4f_{5/2}$ (Pb) and $3d_{5/2}$ and $3d_{3/2}$ (I and Br) doublets due to spin-orbit coupling were 1.33 and 1.50 (\pm 3% error), respectively. The concentration of the different elements (metallic-Pb, I, Br, C and N) relative to Pb²⁺ was estimated from the fitted areas after normalization with the atomic sensitivity factors (ASF).²⁷⁻²⁹

A full extension in details experimental section is deposited as ESI including further details in the calibration of light sources used in this work and MS calibration.

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Graphical Abstract

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