Degradation mechanism of hybrid tin-based perovskite solar cells and the critical role of tin (IV) iodide

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Tin perovskites have emerged as promising alternatives to toxic lead perovskites in next-generation photovoltaics, but their poor environmental stability remains an obstacle towards more competitive performances. Therefore, a full understanding of their decomposition processes is needed to address these stability issues. Herein, we elucidate the degradation mechanism of 2D/3D tin perovskite films based on (PEA)0.2(FA)0.8SnI3 (where PEA is phenylethylammonium and FA is formamidinium). We show that SnI4, a product of the oxygen-induced degradation of tin perovskite, quickly evolves into iodine via the combined action of moisture and oxygen. We identify iodine as a highly aggressive species that can further oxidise the perovskite to more SnI4, establishing a cyclic degradation mechanism. Perovskite stability is then observed to strongly depend on the hole transport layer chosen as the substrate, which is exploited to tackle film degradation. These key insights will enable the future design and optimisation of stable tin-based perovskite optoelectronics.
Hybrid lead halide perovskites remain at the forefront of research activity on next-generation solar cells. Power conversion efficiencies (PCEs) for A\textsubscript{3}I\textsubscript{3} perovskites (where A is typically CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, Cs\textsuperscript{+}, Ge\textsuperscript{2-}, Bi\textsuperscript{3-}, or Sb\textsuperscript{3-}) have evolved from 3.8% to 25.5% within the last decade, surpassing well-established solar cells based on polycrystalline silicon and CuInGaSe\textsubscript{2}. Their outstanding performance is due to their favourable properties such as high carrier diffusion lengths, broad absorption in the visible and near infra-red, and low density of trap states\textsuperscript{3-9}. However, the widespread commercial scaleup of Pb perovskite devices raises concerns in relation to potential health and environmental hazards that their Pb content may cause. As such, this makes the development of Pb-free and environmentally friendly perovskite alternatives a high priority. In order to mitigate the toxicity of Pb-halide perovskites but simultaneously retain their favourable photovoltaic properties, Pb\textsuperscript{2+} can be replaced by lower-toxicity cations with similar outer shell electron configurations, such as Sn\textsuperscript{2+}, Ge\textsuperscript{2+}, Br\textsuperscript{3-} or Sb\textsuperscript{3-}\textsuperscript{10-15}. Among these options, Sn halide perovskites have emerged as the most promising alternatives\textsuperscript{16-29}, exhibiting significantly lower bioavailability compared to Pb-based perovskites\textsuperscript{30} and delivering the highest PCEs among Pb-free perovskite solar cells since devices based on CH\textsubscript{3}NH\textsubscript{3}SnI\textsubscript{3} - Br, were reported in 2014\textsuperscript{10,31}. Interest in these materials also arises from their superior semiconductor properties compared to their Pb analogues, such as broader absorption range, nearly-ideal bandgaps (\textsim\textasciitilde1.3 eV) and higher charge carrier mobilities\textsuperscript{31,32}.

With record PCEs surpassing 13\%\textsuperscript{33}, Sn-based perovskite solar cells have steadily become more competitive due to intensive research efforts. However, the device performance of tin perovskite solar cells has advanced at a slower pace relative to their Pb counterparts, mainly due to their poorer stability under ambient environmental conditions. Such stability issues with these materials relate mainly to the facile oxidation of Sn\textsuperscript{2+} to Sn\textsuperscript{4+}, which is also known to introduce p-type self-doping in the perovskite\textsuperscript{34}. This in turn leads to high rates of monomolecular electron-hole recombination and therefore poor solar cell performance\textsuperscript{35}. A number of strategies have been explored to address these issues, which include the use of Sn\textsubscript{2}X\textsubscript{3} additives to mitigate self-doping\textsuperscript{36,37}, as well as the introduction of inherently more stable low-dimensional phases\textsuperscript{38-46}. However, these approaches do not completely solve the problem and therefore a full elucidation of the decomposition pathways of Sn perovskites is needed to address the stability bottleneck more effectively.

To date, reports describing the degradation mechanism of Sn perovskites remain limited, in contrast with Pb-based analogues\textsuperscript{47-53}. For example, some studies have shown that ASnX\textsubscript{3} (A = Cs\textsuperscript{+}, MA\textsuperscript{+} or FA\textsuperscript{+}; X = I\textsuperscript{-}, Br\textsuperscript{-}) can decompose in air to form A\textsubscript{2}SnX\textsubscript{6} (vacancy-ordered double perovskite\textsuperscript{54}) and SnO\textsubscript{2}\textsuperscript{31,55-57}, while others revealed that FA\textsubscript{3}I\textsubscript{3} and (PEA)\textsubscript{3}SnI\textsubscript{4} (where PEA refers to phenylethylammonium) degrade in the presence of oxygen to SnO\textsubscript{2} and FAI (PEA)\textsubscript{3}SnI\textsubscript{4}\textsuperscript{58,59}. Whilst these findings provide plausible air-mediated degradation routes of Sn-based perovskites, a more detailed understanding of the degradation mechanism as well as knowledge of inconspicuous reaction pathways is required. For example, it is reasonable to suppose that SnI\textsubscript{4} can participate in further degradation reactions of ASnI\textsubscript{3} on account of its high reactivity with water and oxygen relative to FAI, SnO\textsubscript{2} and A\textsubscript{2}SnX\textsubscript{6}\textsuperscript{3,10-15,60-65}. Therefore, a more in-depth understanding of the role of SnI\textsubscript{4} in tin perovskite degradation is necessary.

In this paper, we report on the degradation mechanism of ASnI\textsubscript{3} perovskites (where A represents 20% PEA and 80% FA) under ambient environmental conditions using a combination of diffraction, spectroscopy and ab initio simulation techniques. Herein, we identify SnI\textsubscript{4} as a major contributor to the degradation process and therefore to the instability of such perovskites. Specifically, SnI\textsubscript{4} is a direct product of the decomposition of 2D/3D (PEA)\textsubscript{0.2}(FA)\textsubscript{0.8}SnI\textsubscript{3} under ambient air\textsuperscript{58,59}. We go on to explore the impact of SnI\textsubscript{4} on the optoelectronic properties, solar cell performance and stability of (PEA)\textsubscript{0.2}(FA)\textsubscript{0.8}SnI\textsubscript{3} films. We show that the presence of SnI\textsubscript{4} leads to enhanced non-radiative recombination and poorer device PCE, which is due to high free hole density caused by the introduced Sn\textsuperscript{4+} states. Crucially, we observe that SnI\textsubscript{4}-richer perovskite films degrade faster under ambient conditions, suggesting that SnI\textsubscript{4} accelerates the decomposition of Sn-based perovskites upon exposure to ambient air.

We then investigate the role of SnI\textsubscript{4} in the degradation mechanism of (PEA)\textsubscript{0.2}(FA)\textsubscript{0.8}SnI\textsubscript{3} films and demonstrate that SnI\textsubscript{4} in the film readily evolves to form I\textsubscript{2} via a two-step process, namely, (i) the hydrolysis reaction of SnI\textsubscript{4} with H\textsubscript{2}O to give HI and (ii) the oxidation of HI by O\textsubscript{2} to form I\textsubscript{2}. Interestingly, the perovskite is found to rapidly degrade when exposed to I\textsubscript{2} resulting in the formation of more SnI\textsubscript{4}, thus establishing a cyclic degradation mechanism shown schematically in Fig. 1.

Finally, we find that the stability of (PEA)\textsubscript{0.2}(FA)\textsubscript{0.8}SnI\textsubscript{3} perovskite films are highly dependent on the hole transport layer chosen as a substrate (i.e., NiO\textsubscript{0}, CuSCN and PEDOT:PSS). We observe an improvement in perovskite film stability as the hole withdrawal ability of the bottom layer is increased. We suggest that this process chemically reduces the perovskite film, mitigating the high sensitivity of the Sn-based perovskite to both exogenous and endogenous oxidising species (O\textsubscript{2} and I\textsubscript{2}). Thus, we expect the implementation of highly efficient hole acceptors to provide a pathway towards more stable tin-based perovskite optoelectronics.

![Fig. 1 Proposed cyclic degradation mechanism of a tin iodide perovskite under ambient air exposure.](image)

**Results**

**Degradation in air.** As can be seen in Fig. 1, SnI\textsubscript{4} plays a pivotal role in the degradation of tin iodide perovskites. As such, we first identify the presence of this species as a degradation product of 2D/3D (PEA)\textsubscript{0.2}(FA)\textsubscript{0.8}SnI\textsubscript{3} thin films comparable to those employed in state-of-art solar cells\textsuperscript{39-42,44}. Unless specified otherwise, all degradation experiments reported herein were carried out by exposing samples to ambient air (relative humidity,
of Reaction 1 for FASnI₃ using density functional theory (DFT) simulations, we have calculated an adsorption energy of 0.7 eV. The Sn–O bond length is found to be 2.31 Å, which is close to the experimental Sn–O bond length in SnO₂ (~2.1 Å). We also found that the O–O distance is stretched by over 0.1 Å beyond the bond length of the O₂ molecule; this elongation suggests that the O₂ molecule is likely to be dissociated on the surface and may subsequently participate in the formation of SnO₂ (which is a phase detected in our samples via X-ray photoelectron spectroscopy (XPS); Supplementary Fig. 7 and Supplementary Table 1).

Regarding the thermodynamics of adsorption on the surface, we have calculated an adsorption energy of 0.7 eV. The Sn–O bond length is found to be 2.31 Å, which is close to the experimental Sn–O bond length in SnO₂ (~2.1 Å). The reaction energy is calculated as the difference between the products and the reactants (in which a negative value indicates a favourable exothermic reaction). Details of the simulations and procedures, which have been applied recently to tin halide perovskites, are provided in the Methods section. We calculate a highly favourable energy (~3.46 eV) for Reaction 1, which indicates that the perovskite film indeed degrades in the presence of oxygen as the initial step to form FAI, SnO₂, and SnI₄ in accord with the experimentally observed reaction products.

To examine the microscopic mechanisms of this reaction with oxygen, we also simulated the adsorption of an O₂ molecule on the FASnI₃ perovskite surface. We examined three possible adsorption configurations of an O₂ molecule on the (001) surface with FA/I and Sn/I terminations. We focused on the (001) surface as it has been shown to be one of the most stable and most extensively studied halide perovskite surfaces. In the case of FA/I termination, the O₂ molecule remains at a certain distance from the surface after relaxation independent of the initial configuration showing no interaction with surface species, which indicates that adsorption does not take place (as shown in Supplementary Fig. 22).

For the Sn/I terminated surface, the most stable adsorption configuration of O₂ located right above an Sn atom (for additional views, see Supplementary Fig. 18b). It is clear that one of the oxygen atoms of the O₂ molecule forms a chemical bond with the Sn atom at the Sn/I terminated surface, as shown by the charge density difference in Fig. 2b.

To further complement the experimentally proposed degradation pathways of the Sn perovskite film, we have examined the energetics of Reaction 1 for FASnI₃ using density functional theory (DFT) methods. We note that the FA perovskite system was simulated, rather than including PEA, due to the lack of precise experimental crystal structural data for PEA/FA systems similar to the (PEA)₀₂(FA)₀₈SnI₃ precursor ratio as a reliable starting point and to allow a more focused approach on deriving trends of the reaction and surface properties. The reaction energy is calculated as the difference between the products and the reactants (in which a negative value indicates a favourable exothermic reaction). Details of the simulations and procedures, which have been applied recently to tin halide perovskites, are provided in the Methods section. We calculate a highly favourable energy (~3.46 eV) for Reaction 1, which indicates that the perovskite film indeed degrades in the presence of oxygen as the initial step to form FAI, SnO₂, and SnI₄ in accord with the experimentally observed reaction products.
Our simulation results are therefore consistent with the experimentally proposed Reaction 1 and provide additional atomistic insights into the reaction mechanism of the initial stage in the oxidation of the tin perovskite.

The XRD data in Fig. 2a (bottom panel) show that in the film degraded at room temperature the (100) peak intensity also decreases during the course of an hour as a result of ambient air mediated degradation (relative signal loss vs time: 0% at 0 min, 3% at 30 min, 73% at 60 min; see Supplementary Fig. 1a). In addition, we observe the appearance of a small diffraction peak at 2θ ~ 14.4° (see Fig. 2a, bottom inset, 60 min), which we attribute to the vacancy-ordered double perovskite variant FA₂SnI₆ [17] (see a full pattern after 24 h of exposure to ambient air in Supplementary Fig. 1b). However, the emergence of this phase appears to be delayed as compared to perovskite degradation (12% rise of FA₂SnI₆ peak vs. 73% drop of (PEA)₀.₂(FA)₀.₈SnI₃ peak after 60 min; Supplementary Fig. 3a). This suggests that degradation products formed via Reaction 1 gradually accumulate in the film for a prolonged time (~30–60 min) before triggering the solid-state process between SnI₄ and FAI to form FA₂SnI₆ (Reaction 2)[17,72].

\[
\text{SnI}_4 + 2 \text{Al} \rightarrow \text{Al}_2\text{SnI}_6
\]

(2)

Taken together, the data in Fig. 2 suggest that the presence of FA₂SnI₆ in the film only occurs after substantial perovskite degradation and therefore the early interaction between this phase and (PEA)₀.₂(FA)₀.₈SnI₃ is unlikely. In contrast, it is evident that SnI₄, SnO₂, FAI and PEAI coexist with the tin perovskite in the film during the initial stages of the material decomposition. DFT simulations indicate a very small energy (~0.21 eV) for Reaction 2 involving SnI₄ interacting with FAI to form the FA₂SnI₆ phase, which is consistent with the slower formation of this phase. Upon degrading the sample under heating, we also note that the eventual formation of FA₂SnI₆ is impeded due to the rapid sublimation of SnI₄.

**Optoelectronic and stability effects of tin (IV) iodide.** Next, we examine the effect of SnI₄ on the optoelectronic properties, device performance and ambient stability of (PEA)₀.₂(FA)₀.₈SnI₃ films. For this, the SnI₄ content in the perovskite films was varied by tuning the SnI₄ concentration in the perovskite precursor solution by both thermally purifying the control (commercially sourced) SnI₂ precursor to minimise its SnI₄ impurities and by replacing 2 mol% SnI₄ by both thermally purifying the control (commercially sourced) SnI₂ precursors (Supplementary Fig. 7). Moreover, it is apparent from Fig. 3a that the optical bandgaps of samples (A) and (B) are more notably around 660 and 870 nm, close to the energies of the two main allowed optical transitions in these materials [77]. The high open-circuit voltage (Vₒ) (0.61 V) and fill factor (71%) achieved indicate low trap-mediated recombination and balanced charge transport. However, the relatively low short-circuit current density (Jₛ) is possibly caused by charge losses at perovskite/PEDOT-PSS and/or perovskite/PC₆₀BM interfaces. In contrast, it is evident from J–V data in Fig. 3c that increasing the SnI₄ content in the perovskite layer leads to a significant drop in the PCE (5.23% > 1.73%) due to a drop in Vₒ (0.61 V > 0.55 V) and Jₛ (12.00 mA/cm² > 4.61 mA/cm²); this is consistent with increased carrier recombination and lower carrier mobility as Sn IV⁺ doping is introduced[75,76].

Next, we consider the effect of SnI₄ on the stability of (PEA)₀.₂(FA)₀.₈SnI₃ films. Contour graphs showing normalised absorbance of samples (A), (B) and (C) as a function of time and wavelength are shown in Supplementary Fig. 10. These measurements indicate a drop in absorbance across the spectrum but more notably around 660 and 870 nm, close to the energies of the two main allowed optical transitions in these materials[77]. Normalised absorbance decays at 660 nm are plotted in Fig. 3d for comparison. The data presented in Fig. 3d show that the presence of SnI₄ significantly increases the rate of degradation of (PEA)₀.₂(FA)₀.₈SnI₃ films (stability: sample (A) > sample (B) > sample (C)).

**Evolution of tin (IV) iodide to iodine.** So far, we have shown that: (i) SnI₄ is generated as a product of the oxygen-induced degradation of Sn-based perovskite films and (ii) the presence of SnI₄ in the film is highly detrimental to the optoelectronic properties, device performance and ambient stability of (PEA)₀.₂(FA)₀.₈SnI₃ films. Whilst the deterioration of the optoelectronic properties and photovoltaic performance in the material can be attributed to non-radiative recombination caused by Sn IV⁺ dopants, the role of SnI₄ in the degradation mechanism and stability of Sn perovskites remains unclear. It is reasonable to suppose that SnI₄ can spontaneously evolve into iodine in the presence of moisture and oxygen[1,60–68] as indicated in Fig. 1. This is in agreement with empirical thermodynamic data[78,79].
showing that (i) SnI₄ can hydrolyse to form SnO₂ and HI (Gibbs free energy: $\Delta G^\circ = -0.60$ eV) and, similarly, (ii) HI can react with oxygen to give I₂ and H₂O ($\Delta G^\circ = -2.20$ eV). To investigate whether these reactions are feasible in the perovskites reported herein, a combination of proton nuclear magnetic resonance (1H-NMR) and UV–Visible spectroscopies were used.

First, 1H-NMR spectroscopy is used to analyse the interaction of SnI₄ with moisture in a (PEA)₀.₂(FA)₀.₈SnI₃ film degraded under ambient air for 24 h and dissolved in deuterated DMSO (Fig. 4a). We note that full (downfield) NMR spectra of the solvent, FAI, PEAI, fresh (PEA)₀.₂(FA)₀.₈SnI₃, aged (PEA)₀.₂(FA)₀.₈SnI₃ and their peak assignment are provided in Supplementary Fig. 11, indicating that FA⁺ and PEA⁺ do not undergo any structural alterations within the 24 h degradation period. However, the peak assigned to H₂O traces is detected at ~3.53 ppm in the upfield degraded perovskite spectrum, in contrast with its position at ~3.35 ppm in the reference DMSO-d₆, FAI, PEAI and fresh perovskite spectra (Fig. 4a). The downfield shift in the H₂O peak is indicative of a decrease in electron density around water protons (de-shielding effect), consistent with the protonation of water (i.e., formation of H₃O⁺). The acidification of water is consistent with the formation of HI through the reaction of SnI₄ with H₂O, as detailed in Reaction 38,60,61,63–65:

$$\text{SnI}_4 + 2 \text{H}_2\text{O} \rightarrow 4 \text{HI} + \text{SnO}_2 \quad (3)$$

It is pertinent to note that HI can participate in further reactions under ambient conditions due to its highly reactive nature. For example, HI formed as a result of water-mediated degradation of CH₃NH₃PbI₃ has been suggested to evolve in the air to form I₂. As such, a plausible reaction route for HI oxidation to give I₂ and H₂O is represented in Reaction 4:

$$4 \text{HI} + \text{O}_2 \rightarrow 2 \text{I}_2 + 2 \text{H}_2\text{O} \quad (4)$$

Further evidence for Reactions 3 and 4 occurring was obtained from studying the reaction of water with SnI₄, followed by exposure to air (Supplementary Fig. 12). Specifically, upon the addition of SnI₄ to water, we observe a drop in pH and the precipitation of a white solid, consistent with the formation of HI and SnO₂, respectively. Moreover, ageing this mixture in air leads to a colour change (from clear to yellow/orange) along with new absorption features that indicate the oxidation of HI to I₂ (see Supplementary Fig. 12). We note that the photoinduced decomposition of HI into its elements (H₂ and I₂) cannot be excluded, although we expect this path to be less favourable due to thermodynamic limitations. Taking together, Reactions 3 and 4 suggest that SnI₄ is highly likely to evolve into I₂ through the cooperative action of atmospheric H₂O and O₂, with HI most likely acting as a short-lived, intermediate species. We note that the direct reaction of SnI₄ with O₂ to form I₂ and SnO₂ is also a possibility; nonetheless, this process is known to require high...
temperatures to occur\(^{62}\) and therefore we consider it to be much slower relative to Reactions 3 and 4 combined.

In order to verify the evolution of SnI\(_4\) into I\(_2\) in (PEA)\(_{0.2}\)(FA)\(_{0.8}\)SnI\(_3\) perovskite films under air, we next analyse degraded samples via UV–Visible spectroscopy to detect the halogen. The absorbance spectrum of degradation products extracted via toluene from a film aged in ambient air for 3 weeks is presented in Fig. 4b. The resulting UV–Visible characteristics in Fig. 4b show a shoulder at ~360 nm, assigned to SnI\(_4\), and two further features at ~300 and ~500 nm consistent with the presence of I\(_2\) (see I\(_2\) reference spectrum, Fig. 4b). The elimination of these two features by testing the solution with Na\(_2\)S\(_2\)O\(_3\), which is known to reduce I\(^+\) to I\(^-\), further supports the presence of I\(_2\) as a product of the degradation of SnI\(_4\). We note that the evolution of SnI\(_4\) to I\(_2\) is also observed in toluene solutions (Supplementary Fig. 13).

Perovskite oxidation by iodine. The next question that arises relates to whether iodine can directly react with the perovskite and cause further degradation of the material. To investigate this, we exposed fresh (PEA)\(_{0.2}\)(FA)\(_{0.8}\)SnI\(_3\) films to artificially generated I\(_2\) atmospheres for short periods of time (~350 ppm I\(_2\), ~3 min) and used UV–Visible spectroscopy to study the reaction. Details of the experimental procedure and sample characterisation can be found in ‘Methods’. We find that Sn perovskite films exposed to I\(_2\) vapour result in a dramatic colour change (from black/brown to pale orange, Supplementary Fig. 14) and the absorbance spectrum of degradation products extracted in toluene from an I\(_2\)-exposed film. The absorption peak at ~360 nm reveals once more the presence of SnI\(_4\), confirming that I\(_2\) oxidises the Sn perovskite to SnI\(_4\) (via Reaction 5):

\[
\text{ASnI}_3 + \text{I}_2 \rightarrow \text{SnI}_4 + \text{FAI} \quad (5)
\]

DFT calculations find a favourable energy (–0.61 eV) for this reaction (5) involving I\(_2\) interacting with FASnI\(_3\) to form SnI\(_4\) and FAI, which again agrees with experimental observation. To further analyse the detrimental role of I\(_2\), we also simulated the absorption of an I\(_2\) molecule on the (001) surface of FASnI\(_3\) in a similar methodology to the case of O\(_2\). Figure 4d shows the most stable structure after relaxation on the Sn/I terminated surface, which corresponds to I\(_2\) above the FA molecular cation (for further views, see Supplementary Fig. 20). The top view in Fig. 4d shows that the I\(_2\) molecule forms bridge-like bonds between the Sn and I atoms at the Sn/I terminated surface. The side view shows that the Sn atom that is bonded with one of the I atoms of the molecule is pulled out of the SnI\(_2\) surface, distorting the local regular Sn coordination of the perovskite structure. This suggests that the I\(_2\) species reacts with the perovskite crystal and most likely results in the formation of additional SnI\(_4\) as proposed experimentally in Reaction 5. When the surface is FA/I terminated, the I\(_2\) molecule interacts with the outer iodine atom of the surface and forms a triiodide-like molecular shape, independent of the initial configurations, as shown in Supplementary Fig. 23. Overall, these results show that our simulations are in line with the experimental findings of the cyclic degradation process, as well as providing new mechanistic insights at the atomic level.

Cyclic degradation mechanism of Sn perovskite. Our findings provide a detailed description of the degradation processes in Sn perovskite films under ambient air, as schematically depicted in Fig. 1. The decomposition of the material is triggered by oxygen,
which oxidises the perovskite to SnI$_4$ (Reaction 1). Next, this degradation product can follow two reaction pathways, namely (i) its solid-state evolution to form a vacancy-ordered Sn(IV) double perovskite (Reaction 2) and, more critically, (ii) its evolution in the presence of moisture and oxygen via, most likely, a HI intermediate to give I$_2$ (Reactions 3 and 4), which we find to be a fast process (<10 min; Supplementary Note 1). 

(PEA)$_{0.2}$(FA)$_{0.8}$SnI$_3$ films are found to degrade rapidly (<3 min) when exposed to I$_2$ at lower concentrations than atmospheric O$_2$ (~0.035% I$_2$ < ~21% O$_2$). As can be seen in Fig. 1, SnI$_4$ and I$_2$ can interconvert while causing the decomposition of the perovskite. We believe that our mechanistic insights explain why SnI$_4$ impurities in the perovskite precursor lead to greater premature perovskite degradation (Fig. 3d): the presence of exogenous SnI$_4$ in the perovskite may speed up the formation of highly aggressive I$_2$, which in turns leads to the degradation of the perovskite.

In order to obtain further evidence for our degradation mechanism presented in Fig. 1, we investigated the stability of (PEA)$_{0.2}$(FA)$_{0.8}$SnI$_3$ films in the presence or absence of agents that trigger material decomposition, i.e., O$_2$ and H$_2$O. In these experiments, we exposed the perovskite films to an artificially generated flow of N$_2$ or air under different relative humidity conditions (RH = 0% or RH = 90%) and tracked their optical degradation at 660 nm for a period of 30 min (see Fig. 5). We note that experimental details of these studies are provided in the Methods section. As expected, no degradation is observed when the films are exposed to dry or moist N$_2$ (RH = 0% and RH = 90% respectively). The presence of H$_2$O in the latter may cause hydrolysis of SnI$_4$ impurities in the film to HI via Reaction 3, but O$_2$ is required for the degradation cycle to progress into I$_2$. Moreover, perovskite films exposed to dry air (RH = 0%) show a decay in absorbance that is consistent with the O$_2$-mediated degradation of the material via Reaction 1. However, when the perovskite film is exposed to moist air (RH = 90%) optical degradation becomes much more pronounced, which we attribute to the presence of H$_2$O activating the degradation cycle via Reaction 3. As such, these findings further support the proposed degradation mechanism and highlight the importance of avoiding oxygen and moisture to preserve Sn perovskite stability. We anticipate that the use of highly hydrophobic coatings in perovskite optoelectronic devices (e.g., ultrathin interlayers) will dramatically increase material resilience under ambient conditions, in accordance with the findings detailed here.

**Stabilisation of Sn perovskite films.** We have shown that Sn perovskite films degrade under the oxidative action of atmospheric O$_2$ and endogenously formed I$_2$. These agents chemically decompose the perovskite, causing the oxidation of Sn$^{2+}$ to Sn$^{4+}$ to form SnI$_4$. The details of the mechanism governing the degradation process provided here enable strategies to stabilise the Sn perovskite. As such, the removal of SnI$_4$ and thus Sn$^{4+}$ species from the precursor and film may help delay the perovskite decomposition in air. To further minimise the oxidation of Sn$^{2+}$ to Sn$^{4+}$, it is also important to consider the impact that other layers in the device (e.g., charge transport layers) may have on perovskite stability.

To this end, we explore the influence of the bottom, hole transport materials (HTM) on the stability of ITO/HTM/ (PEA)$_{0.2}$(FA)$_{0.8}$SnI$_3$ samples exposed to air. Specifically, NiO$_x$, CuSCN and PEDOT:PSS were used as HTMs and glass/(PEA)$_{0.2}$(FA)$_{0.8}$SnI$_3$ was employed as a control sample. The samples were exposed to ambient air for 60 min and UV–Visible spectroscopy was employed to monitor degradation. Figure 6a shows the absorbance at 660 nm vs. time. We note that normalised UV–Visible absorption graphs vs. wavelength and
time are presented in Supplementary Fig. 16. From the data presented in Fig. 6a, we observe that the stability of the tin perovskite layer strongly depends on the substrate it is used with. For example, ITO/PEDOT:PSS/perovskite and ITO/CuSCN/perovskite samples exhibit superior stability, followed by the ITO/NiOx/perovskite sample and then glass/perovskite sample.

Next, we discuss the possible origins of this trend. NiOx, CuSCN and PEDOT-PSS have been used as HTMs in high-performance Sn perovskite solar cells. We propose that NiOx, CuSCN and PEDOT-PSS can also accept the excess of dark holes inherently found in the Sn-based perovskite valence band that cause their unwanted p-doping (Fig. 6b). It is plausible that this effect may chemically translate as the reduction of Sn4+ states within the depletion region to Sn2+, which would delay the degradation steps described in Fig. 1 and preserve the Sn perovskite structure for longer. To test the overall ability of HTMs to withdraw holes from the perovskite, we measured the steady-state PL spectra of our samples (Fig. 6c). We observe that perovskite emission is reduced in all perovskite/HTM substrates relative to a perovskite/glass control; this is consistent with PL quenching via photoinduced hole transfer.

More direct evidence for hole transfer was obtained via time-resolved PL spectroscopy (Supplementary Fig. 17); faster charge recombination kinetics is observed in all samples containing HTM substrates, indicating efficient hole transfer from the perovskite. Taken together, the data presented in Fig. 6 suggest that the stability of the tin perovskite layer can be enhanced by improving hole transfer at the perovskite/HTM heterojunction. We note that other factors may also influence stability, such as HTM/perovskite interface passivation, chemical reactivity between HTM and perovskite and substrate-dependent point defect formation. A detailed description of the role of these issues is beyond the scope of the current manuscript and will be reported in future work.

**Discussion**

Using a combination of diffraction, spectroscopy and ab initio simulation techniques, this study provides a greater understanding of the degradation mechanisms in tin perovskites, which is crucial in addressing their stability issues. The present findings illustrate the important role of SnI4 in the optoelectronic properties, device performance and ambient degradation of tin perovskite films based on 2D/3D (PEA)0.2(FA)0.8SnI3. We reveal that SnI4 both as a precursor impurity and as a perovskite degradation product can rapidly evolve in ambient air to form I2, with the latter found to be a highly aggressive species. Specifically, we show that I2 causes the prompt oxidation of perovskite to form additional SnI4 as shown in Fig. 1.

The understanding gained from these new mechanistic insights into the degradation of the Sn-based perovskite (PEA)0.2(FA)0.8SnI3 enables the development of mitigation strategies aimed at reducing its sensitivity towards oxidation. We find that the choice of the bottom HTM substrate can have a significant impact on perovskite film stability. We propose that dark hole withdrawal from the perovskite can cause the chemical reduction of Sn4+ species to Sn2+, which counteracts the oxidation promoted by O2 and thereby delays the formation of SnI4 and its evolution to highly aggressive I2; this ultimately leads to improved stability of the tin perovskite film. In summary, this study sheds new light upon critical features of the degradation mechanism of hybrid tin iodide perovskites, paving the way towards stable and high-performance tin-based perovskite optoelectronics.

**Methods**

**Materials.** All chemicals were purchased from Sigma-Aldrich and used as received unless stated otherwise. Likewise, solvents were acquired from Acros Organics, unless otherwise specified, and used without further purification.

**SnI2 precursor purification.** A SnI2 ampule (99.999%, trace metals basis) was opened under an N2-filled glovebox. The particles of the chemical were crushed in a mortar with a metallic spatula and placed inside a tray which was then put on a hot plate and heated at 250°C for 1 h to eliminate SnI4 via sublimation. After the treatment, SnI2 is kept under dark conditions in a clean vial for future use.

**Substrate preparation.** Glass microscope slides (VWR) were cut into 1.2 cm × 1.2 cm pieces and cleaned in an ultrasonic bath in three 10-min cycles (1: 4% v/v Hellmanex soap in ultrapure water; 2: acetone (VWR); 3: isopropanol (VWR)). Between each step, substrates were thoroughly rinsed with the solvent used in the previous step and then with the solvent to be used in the next step. Next, substrates are dried with a nitrogen gun and treated with UV-light/ozone for 15 min. Substrates are then used directly for perovskite/HTM deposition. ITO substrates (Pisotec, 1.2 cm × 1.2 cm, 15 Ω cm2) were first rinsed with acetone and exposed to the cleaning protocol. After UV/ozone, substrates were used immediately for HTM deposition. PEDOT·PSS (Heraeus Clevios GmbH) was filtered (0.45 μm, PTFE) and deposited via spin-coating at 5000 rpm for 30 s followed by heating at 140°C for 20 min. 300 mg of CuSCN were dissolved in 1 mL of diethyl sulphide (Sigma Aldrich) under stirring for 5 h and filtered (0.45 μm, PTFE), followed by spin-coating at 4000 rpm/40 s. Substrates are then annealed at 300°C for 1 h to obtain NiOx thin films. PMMA coatings required for some perovskite layers were obtained by dissolving 10 mg of the polymer in 1 mL chlorobenzene by heating and stirring at 50°C overnight. The solution is then applied via spin coating (2000 rpm/30 s) onto perovskite films.

**Perovskite thin film preparation.** Under an inert atmosphere, a 4:1 v/v mixture of DMF and DMSO (both ultradry and bottled with molecular sieves) were filtered with 0.2 μm PTFE filters. Next, PEAI (GreatCell Solar), FAI (GreatCell Solar), SnI3 and SnF2 (99%) powders are weighed in a 0.2:0.8:1:0.1 molar ratio, respectively, to obtain 500 μL of a 0.8 M (PEA)0.2(FA)0.8SnI3 perovskite precursor solution by heating and stirring at 70°C for 1 h. The solutions were then filtered (0.2 μm, PTFE) and deposited on the chosen substrate via a two-step spin-coating procedure (1: 1000 rpm/10 s; 2: 5000 rpm/30 s, 800 μL of ultradry toluene are dropped in the middle of the substrate after 12 s), followed by 70°C annealing for 20 min.

**Sample characterisation.** UV–Visible spectroscopy measurements were performed with a Shimadzu UV–2600 integrating-sphere spectrophotometer. Powder XRD patterns were acquired with a PANalytical X’Pert Pro MRD diffractometer by using Cu Ka radiation (λ = 1.5406 Å) and a NIST Si powder as a standard. XPS spectra were measured with a (Jobin Yvon Horiba FluoroMAX-3) spectrophotometer. Time-resolved PL decays (time-correlated single-photon counting) were measured with a Horiba Delftmax Modular Fluorescence Lifetime setup fitted with a PPD 900 detector. The excitation wavelength was chosen at 404 nm or 635 nm (whichever provided the best signal to noise ratio) (Model N–6000; repetition rate pulse duration <200 ps). XPS measurements were performed on ITO/PEDOT·PSS/ (PEA)0.2(FA)0.8SnI3 films using a Thermo KAlpha+ Surface Analysis setup (photon source: Al Ka, 1486.6 eV). Transport of films from the glovebox to the measuring setup was done by using a customised transfer chamber to avoid film exposure to air. Surface scans were made under ultra-humid conditions with no prior etching to avoid unwanted sample reduction. Field-effect and deconvolution were carried out with CasaXPS software. Possible shifts in the acquired spectra were corrected by using the C 1s peak at 284.8 eV. TGA measurements were conducted with a Mettler Toledo Thermogravimetric analyser under an N2 atmosphere at a 5°C/min heating rate. Perovskite film thickness (~250 nm) was measured with an Alpha Step Tencor D500 Surface Profilometer. SEM images were taken with an Leo 1525 Field Emission Scanning Electron Microscope used at 10 kV and fitted with an In-Lens detector. Prior to image acquisition, analysed films were unavoidably exposed to air (~1 min) and coated directly with Cr via sputtering. 1H-NMR and 13C-NMR measurements were taken with a 400 MHz Bruker setup, using TopSpin software.

**1H-NMR sample preparation.** FAI, PEAI, a fresh (PEA)0.8(FA)0.2SnI3 film and a (PEA)0.2(FA)0.8SnI3 film degraded under ambient conditions for 24 h were dissolved separately in a DMSO (VWR)/DMSO-d4 mixture in the glovebox and then sealed into NMR tubes and taken outside for sample measurement.

**I2 detection in fully aged (PEA)0.2(FA)0.8SnI3 films.** The detection of the halogen in toluene via UV–Visible spectroscopy in perovskite films exposed to ambient air for 3 weeks was achieved by previously coating perovskite with PMMA to capture the highly volatile halogen. We note that fully degraded samples are analysed so that I2 does not react rapidly with perovskite as soon as it forms. In consequence, only SnI2 is detected in samples analysed without PMMA coating after shorter exposure times (Supplementary Fig. 15).
Perovskite film exposure to artificial I₂ atmospheres and characterisation. I₂-rich atmospheres were generated by allowing I₂ crystals to rest overnight in the glovebox at the bottom of closed vials containing N₂ only, which allows I₂ to achieve equilibrium vapour pressure. Taking T = 22.9 °C, we estimate the gasogenous I₂ content inside the vials to be ~0.035% (~350 ppm).

Next, (PEA)₂(FA)SnI₃ films were quickly transferred and sealed into the vials containing the I₂ vapours and kept there for a period of 3 min, after which films were removed for their characterisation. Film degradation predictions were extracted via 3 mL toluene in the glovebox (films degraded with I₂ and control fresh films kept in N₂) or in ambient air (films degraded with I₂ and later exposed to ambient air and films degraded under ambient air) for UV–Visible spectroscopy measurements.

Optical degradation tests under dry/moist gas flow. In total, 1.2 cm x 0.6 cm (PEA)₂(FA)SnI₃ films were coated with 100 nm thick Ag electrodes are 20 s. Hundred nanometre-thick Ag electrodes are 20 s. Next, a bathocuproine (BCP) solution in isopropanol (0.5 mg/mL) is used to coat PC60BM at 5000 rpm for 20 s. Hundred nanometre-thick Ag electrodes are then processed via vacuum (10⁻⁵ atm) to achieve equilibrium vapour pressure. Taking the chamber, gas is bubbled through water/glycerol solutions to control humidity (relative humidity in gas flow determined by water/glycerol ratio, as specified elsewhere). Simultaneously, optical degradation of perovskite is tracked by measuring the absorbance of the sealed film every 5 min for a 30 min period.

Device fabrication. PEDOT:PSS is deposited on ITO substrates as specified above and transferred to an N₂-filled glovebox. A (PEA)₃(FA)SnI₃ perovskite solution (0.8 M) made with 9:1 v/v DMF:DMSO is stirred for 1 h at 70 °C and filtered (0.2 μm, PTFE) before film deposition. The solution is applied onto PEDOT:PSS via spin-coating at 4000 rpm for 20 s. The antireflection (500 nm L applied at the tenth second), followed by annealing at 70 °C for 20 min. Next, a 30 mg/mL PC60BM (Ossila solution) in chlorobenzene is deposited at 2000 rpm for 20 s. Next, a bathocuproine (BCP) solution in isopropanol (0.5 mg/mL) is used to coat PC60BM at 5000 rpm for 20 s. Hundred nanometre-thick Ag electrodes are then processed via vacuum (10⁻⁵ mbar) thermal evaporation by using a mask leading to a 0.045 cm² device active area.

Device characterisation. J–V characteristics were measured immediately after fabrication by using simulated AM1.5 solar light (Oriel Instruments) and a Keithley 2400 source metre at a scan rate of 50 mV/s in forwarding bias. Light intensity calibration was carried out with a silicon photodiode. Devices were kept under inert conditions during the measurements by loading them in the glovebox in a homemade measuring chamber.

Computational details. We carried out DFT calculations as implemented in the Quantum ESPRESSO package. For the reaction energies, the Kohn–Sham wave-functions and energies are calculated with the GGA-PBEsol for electronic exchange and correlation, using a plane-wave basis, with energy and charge density cutoffs of 50 and 500 Ry, respectively. Ultrafast pseudopotentials are used to describe the core–valence interactions. The structural relaxation is performed until the force on each atom is smaller than 0.01 eV/Å. The Brillouin zone integration was sampled following the Monkhorst–Pack scheme and convergence with respect to the k-points grid was tested for each compound. For FASnI₃, we have used a supercell of 96 atoms to allow for more degrees of freedom for a low-symmetry structure.

The reactions energies, Eₐ, are calculated as the sum of total energies, E₁₊₂, of the product minus the sum of total energies of the reactants (Eₐ = E₁₊₂ − E₁ − E₂), for each reaction component at the PBE level within the harmonic approximation at 300 K as implemented in the CRYSTAL17 code. Here Eᵢ is the electronic energy corresponding to the DFT total energy at 0 K, Eᵢ is the zero-point energy, Eᵢ is the thermal contribution to the vibrational energy and TS is the entropy contribution. Effective core pseudopotentials were adopted for the heavy atoms Sn (Sn ECp2P865D-411(51)[1G]), and I (1_POB_TZVP-2018) and all-electron Gaussian basis sets for N (N_pob_TZVP-2012), C (C_pob_TZVP-2012), H (H_pob_TZVP-2012) and O (O.8-4111D1G_valenzano-2006) atoms. These basis sets are taken from the online library of the CRYSTAL17 code. For the periodic systems we have used a 2 x 2 x 2 supercell for SnO₂ (320 atoms) and FAI salt (288 atoms), 3 x 3 x 3 supercell for FASnI₃ (324 atoms), and a 4 x 4 x 4 x 4 supercell for SnO₂ (384). We note that the calculated reaction energies with DFT at 0 K are ~4.67 eV, ~0.09 eV, and 0.67 eV for reactions (1), (2), and (5), respectively, which yields similar trends as with the harmonic approximation. We also note that we have used the FASnI₃ system for the calculations of the energies of Reaction (1), instead of the stoichiometric compound PEA₃FAP₃SnI₉, studied in our experiments due to the lack of a well-defined crystal structure from XRD.

For surface calculations, we have cut the FASnI₃ supercell structure along the crystalline plane (001) with Sn/I and FA/I terminations. The resulting slabs have symmetrical equivalent terminations to avoid large dipole effects. To maintain the bulk electronic properties, the slab thickness is chosen to be three times the above supercell of the bulk structure in the out-of-plane direction. To avoid the interaction between the repeated images, the out-of-plane direction of the box containing the slab and the vacuum layer was fixed to 50 Å. The slab without molecules was, first, fully relaxed using the generalised gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formalism for the exchange–correlation. The van der Waals corrections were accounted for using the Grimme dispersion correction DFT-D3. As above, ultrafast pseudopotentials were used for describing the core–valence interactions. The energy and charge density cutoffs were set to 40 Ry and 400 Ry, respectively. The Brillouin zone integration was sampled with a 4 x 4 x 1 k-points grid. Dipole corrections were accounted for to eliminate dipole–dipole interactions between image supercells. For the adsorption of O₂ or I₂ molecules, we have considered three different configurations of the molecules on the FASnI₃ surface, then letting them fully relax. In the case of Sn/I termination, the molecules were initially positioned at distances of 4.5 Å from the Sn/I surface on top of (a) I atom, (b) Sn atom, and (c) FA cation as shown in Supplementary Fig. 18. In the case of FA/I termination, two configurations were considered on top of (a) FA cation and (b) I atom, as shown in Supplementary Fig. 20. The final structures after relaxations are shown in Supplementary Figs. 19 and 20 for O₂ and I₂, respectively. To further examine the sensitivity of the optimised distance between the O₂ molecules and the surface to the initial position before relaxation when the O₂ are placed on top of FA and I (Supplementary Fig. 18a, c), we have manually placed the molecules closer to the surface than the optimised distance. After subsequent relaxation, the molecules were repelled to the optimised positions of the initial relaxation; this indicates that there is no bonding interaction between the O₂ molecule and the FA or I at the surface.

Reporting summary. Further information on experimental design is available in the Nature Research Reporting Summary linked to this paper.

Data availability

The data and computational methods that support the findings of this manuscript are available from the corresponding authors upon reasonable request.

Code availability

The CRYSTAL and Quantum ESPRESSO codes that were used are well established computational materials science codes. Quantum ESPRESSO is a General Public Licensed programme and freely accessible and CRYSTAL is distributed according to specific license terms that are available from the developers.

Received: 10 July 2020; Accepted: 30 March 2021; Published online: 14 May 2021

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Acknowledgements
S.A.H. acknowledges support from EPSRC (grant numbers EP/R020574/1, EP/R023581/1 and EP/R033259/1). L.L. was supported by the EPSRC Centre for Doctoral Training in Plastic Electronics (grant number EP/L016702/1). M.S.I. and N.Z. gratefully acknowledge the EPSRC Grant “Towards Self-scrubbing Stable and Scalable Perovskite Solar Cells” (EP/R020485/1). For supercomputer resources, we thank the GCC/Archer consortium (EP/L000202/1) and Isambard UK National Tier-2 HPC Service operated by GW4 and the UK Met Office and funded by EPSRC (EP/P020224/1).

Author contributions
S.A.H. designed and supervised the experimental project. M.S.I. and N.Z. designed and performed the computational work. L.L. designed experiments, performed sample preparation, spectroscopy and XRD measurements, solar cell fabrication and characterisation, T.G.A. and took photographs of the experimental setup. T.W. carried out sample preparation, spectroscopy measurements, solar cell fabrication and characterisation, T.G.A. and took photographs of the experimental setup. X.L. conducted sample preparation, spectroscopy and XRD measurements and solar cell fabrication and characterisation. D.D. contributed to solar cell fabrication. G.M. performed sample preparation, optical spectroscopy and microscopy measurements and took photographs of the experimental setup. R.J.E.W. contributed to optical spectroscopy measurements and analysis. B.G. provided assistance in optical degradation measurements. T.J.M. conducted solar cell fabrication and characterisation, sample preparation and spectroscopy measurements. T.J.M would like to thank the Royal Commission for the Exhibition of 1851 for their financial support through an 1851 Research Fellowship. L.L., S.A.H., N. Z. and M.S.I. drafted the initial version of the manuscript. All authors contributed to the analysis, discussion and preparation of the final version of the paper.

Competing interests
The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-22864-z.

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Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work.

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