Mixed lead–tin perovskite films with >7 μs charge carrier lifetimes realized by maltol post-treatment†

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Mixed lead–tin (Pb–Sn) halide perovskite films with optimum band gaps near 1.3 eV are promising candidates for next-generation solar cells. However, the performance of solar cells fabricated with Pb–Sn perovskites is restricted by the facile oxidation of Sn(II) to Sn(IV), which induces self-doping. Maltol, a naturally occurring flavor enhancer and strong metal binding agent, was found to effectively suppress Sn(IV) formation and passivate defects in mixed Pb–Sn perovskite films. When used in combination with Sn(IV) scavenging, the maltol surface treatment led to high-quality perovskite films which showed enhanced photoluminescence intensities and charge carrier lifetimes in excess of 7 μs. The scavenging and surface treatments resulted in highly reproducible solar cell devices, with photoconversion efficiencies of up to 21.4% under AM1.5G illumination.

1. Introduction

Lead (Pb)-based perovskite solar cells (PSCs) have reached a power conversion efficiency (PCE) of 25.6%. While such devices are highly optimized, the band gap of Pb-based perovskite materials (Eg > 1.45 eV) actually lies slightly outside the range of maximum performance for single-junction solar cells, 1.1–1.4 eV, as determined by Shockley and Queisser.4 The band gaps of mixed lead–tin (Pb–Sn) perovskite absorbers, meanwhile, fall within the optimal range, being typically 1.2–1.4 eV.5,6 In the last few years, there has been remarkable progress in the development of Pb–Sn PSCS,7–11 with cell efficiencies now reaching 21.7%.12,13 Despite the optimal band gap, however, the reported device efficiencies14–21 remain lower than those of their Pb-based counterparts.1,2,22–24 One of the main impediments for any tin-containing perovskite is the facile oxidation of Sn(II) to Sn(IV). Saidaminov et al.25 and Pascual et al.26 found that the starting material, SnI2, can be easily oxidized, even by the solvent used for the film fabrication (dimethyl sulfoxide, DMSO). Oxygen levels as low as a few ppm can cause Sn(II) in the perovskite films to oxidize, creating Sn(II) vacancies which lead to an increase in hole density.27–30 This p-doping effect has a very strong negative impact on device performance.31

Various strategies for mitigating this issue have been proposed.32 One effective way to reduce the Sn(II) content in the perovskite films is to remove it from the precursor solution, by modifying the perovskite precursor solution via various methods. It was reported that the addition of Sn(II) powder into the Sn-containing precursor solution not only improved the purity of the precursor solution but also reduced Sn(II) vacancies in the resulting perovskite films due to extra Sn(II) generated by the reaction of Sn(II) with metallic Sn(0).33,34 Antioxidants or reducing reagents, like formamidinesulfonic acid,12 pyrazine,35 8-hydroxyquinoline,36 have also been found to reduce the Sn(IV) content in perovskite precursor solution.

It is also important to reduce the Sn(IV) in the starting materials used to prepare the precursor solution. To this end, we have previously developed highly purified starting materials for the fabrication of Sn-based PSCs.37–39 We have also recently reported a Sn(IV) scavenging method based on the high chemical selectivity of an 8π electron system 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine (TM-DHP) for SnF2 over SnI2.40 We found that when TM-DHP is added into a FA0.75MA0.25SnI3 precursor solution in the presence of SnF2, the Sn(II) from SnF2 is reduced to generate Sn(0) nanoparticles. These Sn(0) nanoparticles effectively scavenge Sn(IV) impurities at the precursor preparation stage, giving Sn(IV)-free perovskites in the bulk of the obtained films.

Despite these notable improvements to the quality of the as-fabricated materials, the perovskite films remain vulnerable to oxidation after fabrication, especially at the exposed surfaces.41 To address this, post-treatments for the perovskite films have been developed to protect and passivate the perovskite.
surfaces.43 From a chemical point of view, a strong chelating
agent would be a good choice to stabilize the Sn(II) species. 
Kamarudin et al. reported that amine groups in ethylenedi-
amine bind to the undercoordinated Sn(II) species on the Sn
perovskite surface, resulting in improved stability towards
oxidation.44 Unfortunately, however, the high basicity of the
ethylenediamine resulted in damage to the Sn perovskite
films.44,45 Milder, but effective reagents are therefore desirable
for the post-treatment of the Sn-containing perovskite films.
Among the candidates, the environmental-friendly molecule; 3-
hydroxy-2-methyl-4-pyrene (maltol), known as a ‘flavour enhancer’, is a promising candidate due to its noteworthy metal
chelating ability.46

In this work, we extend the use of the Sn(IV) scavenging
method to mixed Pb–Sn perovskite system, and introduce an
additional post-treatment of the perovskite surface with maltol.
The maltol treatment was found to suppress Sn(II) oxidation and
reduce the density of defects at the perovskite film surface. The
photoluminescence (PL) lifetime increasing from 1.3 to 7.4 μs
accompanied with a fivefold increase in PL intensity. The PCE of
the champion device fabricated with the combination of Sn(IV)
scavenging and maltol post-treatment was 21.4%.

2. Results and discussion

Maltol, C6H6O3, is a small α-hydroxy ketone known for having
an intense chemical activity towards hard metal ions. We found
that the electron-rich oxygen atoms in the carbonyl and the
hydroxyl groups of maltol simultaneously coordinate to the
Sn(II) in SnI2 to form Sn(maltol) complex (Fig. 1a and b).
Similar complexes were observed to form with SnF2 and SnBr2
(Scheme S1 and Fig. S1–S7†). We therefore surmise that if
maltol binds to the undercoordinated Sn(II) sites (Fig. 1c) at the
surface of Pb–Sn perovskite films, it should effectively suppress
the formation of the defects, like Sn(II) vacancies, at the perov-
skite film surface.

To verify this hypothesis, three kinds of perovskite samples
were prepared; control films without scavenging or maltol post
-treatment, films prepared with TM-DHP reductant only, and
films prepared with both TM-DHP reductant and maltol post-
treatment. The perovskite composition used was Cs0.1FA0.6-
MA0.1Sn0.3Pb0.7I3 (FA = formamidinium, MA = methyl-
ammonium). This composition was selected by evaluating the PL
properties and valence band energy levels of a series of 25
candidate materials (Fig. S8 and S9, Table S1†). The perovskite
layers were prepared by the one step method with chloroben-
zene antisolvent. SnF2 (10 mol% with respect to SnI2) and
Pb(SCN)2 (2 mol% with respect to PbI2) were added to the
perovskite precursor solution. SnF2 additive is known to
suppress the oxidation of Sn(II) at the precursor preparation
stage,3 while Pb(SCN)2 is commonly added to mediate the
perovskite crystal growth.19 The precursor concentration is
1.8 M, chosen based on previous reports on efficient mixed Pb–
Sn PSCs.9,18 For the samples with Sn(III) scavenging, 1 mol% TM-
DHP was added to the precursor solution as described previ-
ously.40 For the samples with maltol post treatment, 1 mg mL−1
maltol dissolved in toluene was applied to the surface of the
films by spin-coating, followed by annealing at 65 °C. Accord-
ingly, the control, TM-DHP-treated, and both TM-DHP and
maltol treated perovskite films were respectively prepared.

The oxidation state of Sn at the perovskite film surface was
examined using X-ray photoelectron spectroscopy (XPS). Fig.
2a–c show the Sn 3d signal for the three perovskite films, which
can be deconvoluted into two components; a large main
peak, and a single shoulder on the high binding energy side.
After peak fitting, the main peaks, centered at about 494.8 and
486.3 eV, are assigned to Sn(II), while the secondary features, at
about 496.3 and 487.6 eV, are attributed to Sn(IV). The amount of
Sn(IV) content at the surface of the perovskite films was 9% for
the control, 6% for TM-DHP-treated films, as estimated from
the ratio of the Sn(IV) peak to the total signal area. TM-DHP
effectively scavenges Sn(IV) from the precursor materials,
resulting in less Sn(IV) in the perovskite films. The Sn(IV)
content is reduced further, to 3%, for the TM-DHP and maltol
treated films. The maltol helps to decrease the Sn(IV) content by
protecting and passivating the surface of the perovskite films,
making it more resistant to oxidation by the environment.

The effect of the treatments on the film morphology and
crystallinity were examined by the scanning electron micros-
copy (SEM) and X-ray diffraction (XRD), respectively. No obvious
The reduction in charge carrier recombination is confirmed by the charge carrier lifetimes, which are estimated from the time resolved photoluminescence (TRPL) decay curves shown in Fig. 2f. These measurements were made under a photon flux of $3.5 \times 10^{11}$ photons per cm$^2$, comparable to the incident flux under AM1.5G. The lifetimes were found to depend on the incident light intensity,$^{28}$ as shown in ESI Fig. S12 and S13. With Sn(n) scavenging, the lifetime increased from 1.3 to 3.7 $\mu$s. After maltol post-treatment, the lifetime reached a maximum of 7.4 $\mu$s. This is over six times longer than the value of 1.1 $\mu$s previously reported for mixed Pb–Sn perovskite films.$^7$ This value, obtained for thin polycrystalline Pb–Sn perovskite layers, is even comparable to those reported for state-of-the-art perovskite single crystals.$^{31}$

Diffusion lengths could not be readily determined as we were unable to estimate the charge carrier mobility from the space-charge-limited current data.$^{32}$ Instead, an approximate evaluation of the diffusion length was realized using reported values for the diffusion coefficients ($D$) of Pb–Sn perovskite.$^7$ Using the PL lifetime, $t = 7.4 \mu$s, determined for our film, and their reported values of 0.02–0.05 cm$^2$ s$^{-1}$ for the diffusion coefficients, the carrier diffusion length calculated from $\sqrt{Dt}$, is estimated to fall in the range of 3.8–6.1 $\mu$m. The local mobility of the holes and electrons within individual perovskite grains can be estimated using flash-photolysis time-resolved microwave conductivity (TRMC) (Fig. S14 and S15).$^{33,34}$ The values are estimated to be 70 cm$^2$ V$^{-1}$ s$^{-1}$ and 110 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. These high values point to the overall high quality of the perovskite
materials, which is also supported by the XRD and PL experiments.

To confirm the impact of the improved charge carrier recombination dynamics on the device performance, the corresponding PSCs were fabricated. The solar cells had an positive–intrinsic–negative structure: fluorine-doped tin oxide (FTO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/perovskite/fullerene (C60)/bathocuproine (BCP)/ silver (Ag) (Fig. 3a). The perovskite film thickness was 800–1000 nm. The current density–voltage (J–V) curves of the best devices are shown in Fig. 3b, and the corresponding photovoltaic parameters are listed in Table 1. Measurements were made in inert atmosphere, under AM1.5G simulated solar radiation.

For control devices prepared without the TM-DHP or maltol treatment, the highest PCE was 18.2% (forward scan, $J_{SC}=31.1$ mA cm$^{-2}$, $V_{OC}=0.78$ V, and FF = 0.75). With the TM-DHP but without maltol treatment, the forward scan $J_{SC}$, $V_{OC}$, and FF was slightly increased to 31.6 mA cm$^{-2}$, 0.79 V, and 0.76, respectively, and the PCE reached 19.0%. Significantly improved performance was achieved when, in addition to TM-DHP treatment, the perovskite layers were post-treated with maltol. The champion PCE was 21.4% (reverse scan, $J_{SC}=33.1$ mA cm$^{-2}$, $V_{OC}=0.82$ V, and FF = 0.79) and devices had considerably improved reproducibility (Fig. S16†). This PCE is very close to the reported best performance for mixed Pb–Sn PSCs, 21.7%.12,13

In Fig. 3c, we can observe that the PSCs reached the highest external quantum efficiency (EQE) of 91.2% at 680 nm, and the corresponding internal quantum efficiency (IQE) was 98.8%. The integrated $J_{SC}$ was 32.3 mA cm$^{-2}$, somewhat lower than the maximum value (33.2 mA cm$^{-2}$) obtained from the $J$–$V$ curves. The difference is attributed to the spectral mismatch of the solar simulator especially in near-infrared region. Considering the mismatch factor, which was calculated to be 1.027 (Fig. S17†), the $J_{SC}$ values from the $J$–$V$ curves correspond closely with the integrated value.

To investigate the improved device performance in the view of its electronic properties, additional characterizations of the devices were performed. Impedance scans (Fig. 3d and S18†) reveal a single semicircle for each device, the diameter of which

| Table 1 | Photovoltaic parameters of the perovskite solar cells |
|---------|-------------------------------------------|
| Device  | Scan$^a$ | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) |
| Control | Forward | 31.1 | 0.78 | 0.75 | 18.2 |
|         | Reverse | 30.9 | 0.78 | 0.74 | 18.1 |
| TM-DHP  | Forward | 31.6 | 0.79 | 0.76 | 19.0 |
|         | Reverse | 31.3 | 0.80 | 0.75 | 18.7 |
| TM-DHP + maltol | Forward | 33.2 | 0.82 | 0.77 | 21.0 |
|         | Reverse | 33.1 | 0.82 | 0.79 | 21.4 |

$^a$ Scan direction: forward and reverse denotes the scan direction from $J_{SC}$ to $V_{OC}$ and from $V_{OC}$ to $J_{SC}$, respectively.

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Fig. 3 (a) Schematic illustration and cross-sectional SEM image of a completed device with the architecture of FTO/PEDOT:PSS/perovskite/C60/BCP/Ag. (b) $J$–$V$ curves of the PSCs. (c) IQE, EQE, reflectance spectra and integrated $J_{SC}$ of the encapsulated champion device under AM1.5G illumination in ambient air, no antireflection technique was applied for the device fabrication. (d) Complex impedance plots of PSCs measured in inert atmosphere under AM1.5G illumination. The shunt resistance across the perovskite layer was estimated at 93, 318, and 550 $\Omega$ cm$^2$ for the control, TM-DHP, and both TM-DHP and maltol treated PSCs, respectively. (e) The open-circuit voltage $V_{OC}$ as a function of illumination intensity with an ideality factor of 1.62, 1.60, and 1.50 for the control, TM-DHP, and both TM-DHP and maltol treated PSCs, respectively. Insert shows the equivalent circuit model for fitting the electrolyte-chemical impedance spectroscopy data. (f) Dark current–voltage curves of the hole-only devices with the architecture of FTO/PEDOT:PSS/perovskite/PTAA/Ag. PTAA is poly(triaryl amine).
Charge carrier recombination mechanisms are reflected by the Shockley diode ideality factor, as determined by the slope of the plot of $V_{OC}$ versus incident light-intensity (Fig. 3e). The ideality factor is 1.62, 1.60 for the control and TM-DHP treated devices, respectively, and falling to 1.50 for the device treated with both TM-DHP and maltol, indicating lower non-radiative (trap-mediated) recombination rates in the maltol-treated PSCs.

To estimate the density of trap states in the films, we measured the dark current–voltage ($I$–$V$) curves of the hole-only and electron-only devices (Fig. 3f). The voltage where the current begins to sharply increase can be assigned to the trap-filled limit voltage ($V_{TFL}$). $V_{TFL}$ is related to the trap density, $N_{trap}$, as $V_{TFL} = N_{trap}eL^2/(2εrε_0)$, where $ε$ is the elementary charge of the electron, $ε_0$ is the vacuum permittivity, $ε_r$ is the relative dielectric constant of the perovskite (around 32), and $L$ is the thickness of the perovskite film. $V_{TFL}$ for the perovskite films in the hole-only devices is 0.62, 0.54, and 0.14 V, respectively, corresponding to trap densities of $2.9 \times 10^{13}$, $2.4 \times 10^{15}$, and $6.3 \times 10^{14}$ cm$^{-3}$. The electron trap densities for the perovskite films modified with TM-DHP and maltol were estimated to be around $3.6 \times 10^{14}$ cm$^{-3}$ (Table S2, Fig. S19). These electrical measurements confirm the lower trap-state densities in the treated perovskite films, which leads to longer carrier lifetimes of the treated perovskite films, as well as improved performance of the PSCs.

3. Conclusions

In this study, we found that maltol, a cheap and common flavor enhancer, can coordinate to Sn($n$) in SnI$_2$ to form a stable complex (SnI[maltol]). Based on this strong affinity of maltol for Sn($n$), we demonstrated that, when used in combination with a Sn($n$) scavenging method acting on the precursor solution, post-treatment with maltol leads to suppressed Sn($n$) content, decreased defect densities, and remarkably prolonged charge carrier lifetimes in the perovskite films, over 7 µs. A PCE of 21.4% was achieved for the champion solar cell. These high quality Pb–Sn materials achieved by the simple post-treatment should be useful for wide variety of optoelectronic devices.

Author contributions

S. H. and A. W. conceived the idea. S. H. and K. O. performed the synthesis and characterization of Sn complexes. S. H. and M. A. T. conducted the XPS measurements. K. O. conducted the XRD measurements. K. O. carried out the PL measurements. R. M. conducted the impedance measurements. S. H. conducted the SCLC measurements with the help of R. M. M. A. T. and K. O. carried out the NMR measurements. S. H., M. A. T., R. M., and A. W. prepared the manuscript. All authors commented on the manuscript. A. W. supervised the project.

Conflicts of interest

There are no conflicts to declare.

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