Synergistic improvements in stability and performance of lead iodide perovskite solar cells incorporating salt additives†

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The main issues in planar perovskite solar cells are the coverage and crystallinity of the perovskite film on the PEDOT:PSS layer. To enhance these features, we introduced alkali metal halides (salts) as additives into the perovskite precursor solution used in a two-step preparation method. These alkali metal halides chelate with Pb2+ ions and enhance the crystal growth of PbI2 films, resulting in nanostructured morphologies. The nanostructured PbI2 films promote homogeneous nucleation and larger crystallite sizes, thereby enhancing the morphology and crystallinity of the perovskite films. The alkali metal halides recrystallize the small grains and passivate the grain boundaries and interface states, allowing effective charge generation and dissociation in perovskite films. Photoluminescence measurements indicated that perovskite films prepared with salt additives featured fewer charge traps and defects. The power conversion efficiency of the device incorporating a small amount of a salt additive increased by approximately 33%—from 11.4 to 15.08%. This device was more stable than a corresponding device prepared without the additive, with only 16.5% degradation occurring over a period of 50 days.

Introduction

Organometal halide perovskites are emerging materials in photovoltaics (PVs), light emitting diodes,9–12 and lasers13,14 because of their high absorption coefficients, long carrier life times, micrometer diffusion lengths, high fluorescence yields, and wavelength tunability.5,11,12,15–17 Indeed, an exceptionally high solar cell performance of 20.2% has been achieved when using a solution-processed lead halide perovskite.18 Two kinds of device architectures have been used in perovskite solar devices: mesoporous5,19 and planar heterojunctions.6,19–21 High temperature annealing is required to make crystalline TiO2 layers in mesoporous-type solar cells, whereas planar heterojunction-based solar cells can be fabricated at low temperature—more suitable for roll-to-roll manufacturing of large-area, flexible solar cells.8,22 Unlike mesoporous-type devices, in which the perovskite material can infiltrate within the porous matrices, perovskite films with pinholes and non-uniform coverage are usually present in planar-type perovskite solar cells; these factors are mainly responsible for their poor device performance.

Controlling the morphology and crystallization of perovskite thin films in planar architectures is a main challenge affecting our ability to develop high-performance devices.21–25 These features are determined by their thermodynamics and growth kinetics, and can be controlled by varying the thin film fabrication process, the choice of solvent, the annealing temperature, and the levels of moisture and processing additives. Several thin film fabrication processes, including spin coating, dip coating, spray coating, blade coating, and thermal evaporation, have been investigated to control perovskite film formation.4,24,26–29 Two-step perovskite thin film preparation has been superior to single-step formation when attempting to obtain continuous and pinhole-free films. Recently, incorporation of additives in the perovskite solution process has become a simple way to improve the film coverage and crystallinity. Several additives, including NH4Cl, 1,8-diiodooctane, 1-chloronaphthalene, polyvinylpyrrolidone, hydroiodic acid (HI), and hydrochloric acid, can be used to form smooth, continuous, and uniform films with flawless perovskite nanocrystals, significantly improving the device performance.29–31

In this study, we investigated the influence of alkali metal halides as additives on the performance of perovskite solar cells. We incorporated alkali metal halides into the lead iodide (PbI2) precursor solution to tune the morphology of the resulting PbI2 films. These halogenated additives chelate with Pb2+...
ions during film formation, thereby enhancing crystal growth and morphology. Tuning the PbI$_2$ morphology led to significant improvements in the perovskite morphology and crystallinity when using the two-step preparation method. The highly crystalline, large-crystal-sized perovskite formed in the presence of alkali metal halide additives resulted in a power conversion efficiency (PCE) of 15.08% for the resulting planar heterojunction perovskite solar cell.

Results and discussion

We fabricated devices having the architecture glass/ITO/PEDOT:PSS/perovskite/PC$_{61}$BM/C$_{60}$/BCP/Al and investigated their PV performance. Here, we used C$_{60}$ to minimize the trap densities. Fig. 1a and b display photocurrent density–voltage ($J$–$V$) and external quantum efficiency (EQE) curves of perovskite solar cells prepared in the presence and absence of different alkali metal halide additives (at their optimized concentrations); Table 1 lists the corresponding photovoltaic parameters. No delay time existed between the measurement voltage points for any of the $J$–$V$ measurements. Each solar cell performance was measured using an aperture metal mask having an active area of 10 mm$^2$. Fig. S1† presents the $J$–$V$ characteristics of devices prepared with KCl at concentrations varying from 0.5 to 1%, NaCl varying from 0.75 to 1.25%, and LiCl varying from 0.25 to 0.75%; Table S1† lists the corresponding photovoltaic parameters. The device prepared with 0.75% KCl achieved the highest PCE (15.08%), with a short-circuit current density ($J_{sc}$) of 19.42 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 1.04 V, and a fill factor (FF) of 74.67%. Lower (0.25%) and higher (1%) concentrations of KCl also resulted in PCEs (12.05 and 12.72%, respectively) higher than that (11.40%) of the device prepared without any additives. Similarly, the device prepared using 1% NaCl as the additive also showed improved device performance: a PCE of 12.77% with a value of $J_{sc}$ of 17.59 mA cm$^{-2}$, a value of $V_{oc}$ of 0.96 V, and the highest FF measured in this study (75.62%). A higher concentration of NaCl resulted in a dramatic decrease in the values of $V_{oc}$ and $J_{sc}$, leading to a poor PCE of 9.54%. The presence of LiCl as the additive at all tested concentrations suppressed the device performance relative to that of the device prepared without any additives. The lowest tested concentration of LiCl (0.25%) gave a device performance

<table>
<thead>
<tr>
<th>Salt</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75% KCl</td>
<td>1.04</td>
<td>19.42</td>
<td>18.33</td>
<td>74.67</td>
<td>15.08$^a$ (14.12)$^b$</td>
</tr>
<tr>
<td>1% NaCl</td>
<td>0.96</td>
<td>17.59</td>
<td>16.76</td>
<td>75.62</td>
<td>12.77$^a$ (12.14)$^b$</td>
</tr>
<tr>
<td>0.25% LiCl</td>
<td>0.91</td>
<td>15.97</td>
<td>15.24</td>
<td>68.67</td>
<td>9.98$^a$ (9.35)$^b$</td>
</tr>
<tr>
<td>Without salt</td>
<td>0.90</td>
<td>16.60</td>
<td>15.88</td>
<td>76.31</td>
<td>11.40$^a$ (10.86)$^b$</td>
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</table>

$^a$ Best device performance. $^b$ Average performance from 10 devices. $^c$ Measured $J_{sc}$ values from the solar simulator. $^d$ Integrated $J_{sc}$ values from the EQE measurement.

19.42 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 1.04 V, and a fill factor (FF) of 74.67%. Lower (0.25%) and higher (1%) concentrations of KCl also resulted in PCEs (12.05 and 12.72%, respectively) higher than that (11.40%) of the device prepared without any additives. Similarly, the device prepared using 1% NaCl as the additive also showed improved device performance: a PCE of 12.77% with a value of $J_{sc}$ of 17.59 mA cm$^{-2}$, a value of $V_{oc}$ of 0.96 V, and the highest FF measured in this study (75.62%). A higher concentration of NaCl resulted in a dramatic decrease in the values of $V_{oc}$ and $J_{sc}$, leading to a poor PCE of 9.54%. The presence of LiCl as the additive at all tested concentrations suppressed the device performance relative to that of the device prepared without any additives. The lowest tested concentration of LiCl (0.25%) gave a device performance

Fig. 1 $J$–$V$ characteristics of perovskite solar cells. (a) Photo- and dark currents. (b) EQE spectra of device prepared using various salt additives. (c) Champion device performance. (d) Influence of the scanning direction on the performance of the perovskite solar cell prepared with KCl as the additive.
of 9.98%, with a value of $J_{sc}$ of 15.97 mA cm$^{-2}$, a value of $V_{oc}$ of 0.91 V, and a FF of 68.67%. We suspect that this behavior was due to the high oxygen- and moisture-sensitivities of Li$^+$ ions, as confirmed by the presence of a strong O 1s peak in X-ray photoelectron spectroscopy (XPS) spectra. For comparison, Table S2 provides a literature survey of the additives that have been used previously in perovskite solar cells. Compared with all of the reported additive-based perovskite solar cells, the device prepared using KCl as the additive provided the best performance. These alkali metal halide additives were acting as electrically active impurities that recrystallized the small grains and passivated the grain boundaries and interface states, thereby allowing effective charge generation and dissociation in the perovskite films.  

Fig. 1 presents EQE spectra of the perovskites formed with and without the various additives at their optimized concentrations. The additive-containing devices displayed broader and improved EQEs from 350 to 800 nm, relative to those prepared without additives. A dimple appeared near 600 nm in the EQE spectra, due to the strong reflection of glass/ITO at this wavelength. The EQE of the top-performing KCl-based device reached over 85%, whereas that of the device prepared without additives reached only 70%. We attribute the improvement in EQE mainly to the better morphology and crystallinity of the perovskite film. The PCE of the optimal device prepared using 0.75% KCl as the additive (15.08%) was approximately 33% higher than that (11.40%) of the device prepared without any additive (Fig. 1c). Photocurrent hysteresis exists in many perovskite solar cells, interfering with an accurate measurement of device efficiencies.  

To determine whether photocurrent hysteresis existed in our devices, we measured the device performance in both forward and reverse sweep directions. Fig. 1d reveals no obvious photocurrent hysteresis in our optimized device in either sweep direction. Photocurrent hysteresis arises mainly from the formation of traps in lead halide perovskite materials. An optimized device structure and film formation process can significantly decrease photocurrent hysteresis. Here, we formed continuous, compact, crystalline perovskite films by adding additives and using PC$_{60}$BM as a passivation layer to minimize trap densities. Perovskite films were prepared through sequential spin-coating of PbI$_2$/salt mixtures (using LiCl, NaCl, and KCl at different weight percentages) and MAI onto PEDOT:PSS to test the effects of the different salts as additives on the morphology, crystallinity, and stability of the films. Fig. 2 displays the absorption and photoluminescence (PL) spectra of the perovskite films prepared with and without the salt additives. The perovskite thin films incorporating the alkali metal halides exhibited increased light absorbance at wavelengths from the visible to the near-infrared, due to their relatively greater surface coverage and uniformity of their films. The increase of band edge absorption near 760 nm was consistent with the increased crystallinity of the perovskites processed using the salt additives. The absorption of the perovskite thin film prepared using 0.75% KCl was greater than that of the films prepared using LiCl and NaCl. For the PL measurements, all of the samples were prepared on glass substrates to avoid quenching at the interfaces. The PL intensities of the perovskite thin films prepared with the salt additives were higher than those of the films prepared without any additive, because of the higher crystallinity of the former. A compact and crystalline film will absorb more light and generate more excitons and, thereby, produce a higher PL emission. The PL intensity of the perovskite thin film doped with 0.75% KCl was almost double that of the device prepared without any additives, implying that a crystalline and uniform film was an important aspect for generating a greater number of charge carriers (excitons).

For X-ray diffraction (XRD) measurements, we prepared perovskite films, with and without alkali metal halides as additives, on glass substrates using a two-step spin-coating method. Fig. 3a reveals peaks at values of 2$\theta$ of 14.2, 24.6, 28.5, and 31.98$^\circ$ corresponding to the (002), (202), (004) and (310) planes, respectively, confirming the formation of a tetrahedral perovskite crystal structure. The peak positions are consistent with the reported results; no secondary phases appeared arising from other species (e.g., PbI$_2$ or MAI). The intensities of the perovskite peaks were enhanced significantly when using the alkali metal halides as additives, suggesting the formation of highly crystalline perovskite films. The crystallinities of the perovskite films improved for all three additives at specific concentrations (Fig. S2†). To further investigate the perovskite crystallinity, we calculated the size of the perovskite crystals from the full width at half maximum (FWHM) of the signal at a value of 2$\theta$ of 14.2$^\circ$ (Fig. 3b). We estimated the average crystal size using the Scherrer eqn (1)

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$  

where $D$ is the crystallite size, $\lambda$ is the wavelength of the X-rays, $\beta$ is the FWHM of the diffraction peak, and $\theta$ is the diffraction angle; the factor 0.89 is the shape factor that is a characteristic of a certain particle. The crystallite sizes of the perovskites prepared without any additive and with 0.75% KCl, 1% NaCl, and 0.25% LiCl were 253 ± 20, 468 ± 50, 384 ± 40, and 422 ± 40 nm, respectively. The crystallinity and crystallite size of the perovskite film prepared with 0.75% KCl as the additive were greater than those of the films prepared with the other additives; these factors were mainly responsible for the significant enhancement in PCE.
To understand the effects of the additives on the PbI$_2$ and perovskite morphologies, we used a scanning electron microscope (SEM) to analyze the films prepared with and without them. Perovskite films with excellent uniformity and large crystal sizes can be obtained through careful control of the nucleation and growth processes.\textsuperscript{31} The procedure we used for the preparation of the perovskite films for SEM analysis was identical to that used for device fabrication. Fig. 4a–d present SEM images of the spin-coated PbI$_2$ films prepared with and without the additives; Fig. 4e–h show the perovskite films prepared with and without additives. In this two-step method, the quality of the perovskite film depends strongly on the quality of the precursor PbI$_2$ film. The spin-coated PbI$_2$ film (Fig. 4a) prepared without any additive was non-continuous and accompanied by many small pinholes. A non-continuous PbI$_2$ film will form a poorly crystalline, small-crystallite perovskite film that will significantly decrease device performance.

The PbI$_2$ films formed with the salt additives featured nanostructured morphologies: rod shapes for 0.75% KCl and 1% NaCl and disc shapes for 0.25% LiCl. These nanostructures presumably had a great influence on the formation of high-quality, uniform, crystalline perovskite films after the spin-coating of MAI onto their surfaces. The film prepared using 0.75% KCl as the additive featured more uniform and dense nanocrystals of large grain size than did those films prepared using 1% NaCl or 0.25% LiCl. Larger grains would minimize the permeability of oxygen and moisture and, thereby, enhance the stability of the resulting device. In addition, the uniform coverage of the film played an important role in improving interfacial contact, allowing efficient charge transfer and minimizing exciton recombination.

We recorded XPS spectra to investigate the changes in binding energy of the perovskite core level peaks in the presence and absence of salt additives (Fig. 5). For XPS analysis, all of our samples were prepared on ITO/PEDOT:PSS substrates. The samples of perovskite prepared with and without the additives displayed core level peaks for lead, iodine, carbon, nitrogen, and oxygen atoms. The binding energies of the lead, iodine, carbon, and nitrogen atoms were not affected by the presence of small amounts of the additives. In contrast, the perovskite...
prepared using 0.25% LiCl displayed a sharp O 1s peak at 531.4 eV, which did not appear for the other additive-containing perovskites, possibly because of the high oxidation rate of Li+. Fig. S3† presents the binding energies of the K 2p3, Na 1s, and Li 1s core level peaks. Peaks at binding energies of 293.2 and 1071.8 eV corresponded to the K+ and Na+ ions, respectively. No peak appeared for Li 1s, however, due to its very low sensitivity, even when increasing the number of scans for acquiring the Li 1s spectrum. To investigate the presence of Cl in our perovskite films, we also measured the binding energy of the Cl 2p core level peak (Fig. S3d†). We found no evidence for the presence of Cl atoms at the surfaces of the perovskite films formed with the additives, suggesting either evaporation of Cl atoms during annealing of the perovskite films or the presence of only small amounts that could not be identified because of the limitations of the XPS instrument.

The stability of perovskite solar cells is an important issue affecting their potential applications. Accordingly, we investigated the stability of our perovskite devices prepared with and without KCl (0.75%) as an additive. We stored the unencapsulated devices inside a glove box (oxygen: 15 ppm; water: 0.1 ppm) for 50 days and then tested their performance. Fig. 6 presents their normalized PCEs over time. The stability of the device prepared with the KCl additive was better than that of the device prepared without the additive, due to the formation of a more compact film with larger crystallites. The KCl-added perovskite device exhibited long-term stability: only 16.5% degradation over 50 days under storage in a dark environment. It is possible that its degradation arose from the transport layer (C60/BCP) or at the ITO/PEDOT:PSS interface. The inset to Fig. 6 presents photographs of the perovskite films in air over time. The perovskite film prepared without the salt additive began to degrade to a yellow color after 5 days, whereas the color change of the film prepared with the salt additive did not occur for over 20 days. The device stability of the perovskite film under continuous light shocking conditions (6 h per day) was also measured and it is shown in Fig. S4.† The device without additives showed complete degradation after 35 h exposure and meantime the device with the KCl additive showed significant improvement in stability, retaining 56% of its initial efficiency after 100 h exposure time. The origin of the improvement is possibly due to the recrystallization of small grains and passivation of grain boundaries by salt ions.

To further investigate the charge carrier transport process in perovskite devices, electrochemical impedance spectroscopy (EIS) was carried out to measure the perovskite device with and without salt additives. Fig. 7 shows the Nyquist plots of the perovskite with and without salt additives under AM1.5G 1 sun illumination and at the applied voltage close to the device $V_{oc}$. The resistance decreases for the perovskite devices with KCl and NaCl additives compared to those without additives. It indicates

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**Fig. 5** XPS spectra of perovskite films prepared with and without salt additives (KCl, NaCl, and LiCl). (a) Survey, (b) Pb 4f7, (c) I 3d5, (d) C 1s, (e) N 1s and (f) O 1s.

**Fig. 6** Normalized PCEs, over time, of perovskite solar cells prepared with and without KCl as an additive. Inset: photographic images of the color changes of the perovskite films in air over time.
the smoother carrier movement inside the perovskite film results in reduced traps and resistive losses. The defects in the perovskite film were reduced by adding KCl and NaCl additives thus leading to less recombination and better device performance. In contrast, the device with LiCl exhibits severe resistance which led to poor device performance.

**Conclusion**

A significant enhancement (ca. 33%) in PCE, from 11.40 to 15.08%, occurs after incorporating a small amount of KCl as an additive into a planar heterojunction perovskite solar cell. In the presence of alkali metal salts, PbI₂ films exhibited nanostructured (rod, disc) morphologies that greatly influenced the formation of high-quality, uniform perovskite films after spin-coating MAI onto their surfaces. The additives improved the crystallinity and morphology of the perovskite films and, thereby, enhanced their absorption and exciton generation. Perovskite films fabricated using KCl as the additive had larger crystals and a more compact morphology, relative to those prepared using NaCl and LiCl, leading to greater device performance. A device prepared with KCl as the additive displayed long-term stability; only 16.5% degradation occurred over a period of 50 days under storage in a dark environment. This approach using rational additives opens up a new path for enhancing the performance and stability of perovskite solar cells.

**Acknowledgements**

Dr Chu acknowledges the Ministry of Science and Technology (MOST) of Taiwan (104-2221-E-001-014-MY3 and 104-2221-E-009-096-MY3) and the Career Development Award of Academia Sinica, Taiwan (103-CDA-M01), for financial support.

**Notes and references**


