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An 80.11% FF record achieved for perovskite solar cells by using the NH_4Cl additive†

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The light-absorbing perovskite layer fabricated using the NH_4Cl additive shows high crystallinity and better morphology. The resulting solar cells gave a decent power conversion efficiency of 9.93% and a fill factor record of 80.11%. This work provides a very simple but effective approach to enhance the power conversion efficiency of perovskite solar cells.

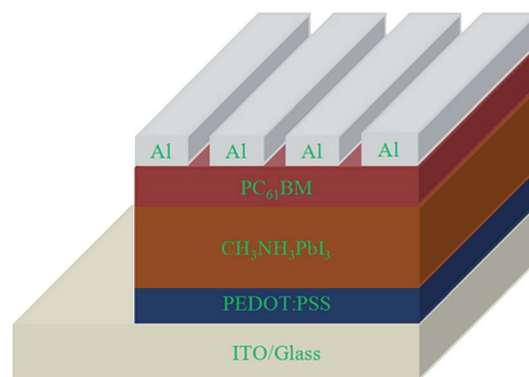
Perovskite solar cells using organometal halide perovskites as light-absorbing materials have received a great deal of attention due to their excellent photovoltaic performance.^{1–4} $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{I}$) perovskite nanocrystals were used as sensitizers in dye-sensitized solar cells (DSSCs) and a power conversion efficiency (PCE) of 3.8% was obtained in 2009.⁵ Later, Park *et al.* reported an improved PCE of 6.54% by using $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals in DSSCs.⁶ In solid-state hybrid solar cells, PCEs of 10.9% and 9.7% were achieved when $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ were used as the absorbers, respectively.^{1,2} Recently, Wojciechowski *et al.* reported a 15.9% PCE in meso-superstructured perovskite solar cells.⁷ Perovskites are excellent semiconductors in solar cells due to their panchromatic light absorption, ambipolar transport and very long electron/hole diffusion lengths.^{8,9} A great deal of effort has been paid by researchers to explore this brand-new solar cell, *e.g.* developing low-temperature fabrication methods,⁴ making new hole conductors¹⁰ and trying flexible substrates.¹¹

Perovskite solar cells with device structure indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/perovskite/[6,6]-phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM)/Al are becoming popular because they can be made into flexible devices and processed at 150 °C.^{11–16} Malinkiewicz *et al.* sandwiched sublimated $\text{CH}_3\text{NH}_3\text{PbI}_3$ between the organic hole-transport layer and PC_{61}BM , and obtained a 12% PCE.¹⁵ Lam *et al.* developed solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ /

PC_{61}BM solar cells and obtained a 5.2% PCE using a one-step deposition method and a 7.4% PCE using a sequential deposition method.¹³ Kim *et al.* improved the morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer using solvent mixtures and obtained a PCE of 6.2%.¹⁶ The crystallinity and morphology of perovskite layers are very important for the performance of perovskite solar cells.^{16,17}

Here, we report an innovative approach by using chloride additives to improve the crystallinity and morphology of perovskite layers, and the performance of solar cells. The effects of $\text{CH}_3\text{NH}_3\text{Cl}$ and NH_4Cl additives on the crystallinity and morphology of perovskite layers were studied. The additives helped to form flawless perovskite nanocrystals and also helped to form smooth and uniform films, leading to better device performance. A solution-processed device with the structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ / PC_{61}BM /Al was studied. The device fabricated using NH_4Cl as an additive gave a PCE around 10% and a fill factor (FF) over 80%.

The structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ / PC_{61}BM solar cells is shown in Fig. 1. PC_{61}BM is often used as an electron acceptor in organic solar cells and it can effectively quench the photoluminescence of perovskites in a bi-layer structure.¹⁸ So PC_{61}BM can act as an electron acceptor and electron collection layer in perovskite

Fig. 1 Structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ / PC_{61}BM solar cells.

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solar cells. Under illumination, excitons generated in the perovskite layer will dissociate at the perovskite/PC₆₁BM interface.^{14,18} Electrons move to the LUMO of PC₆₁BM and are collected by the Al electrode. PEDOT is used as a hole-transport layer, holes move to the PEDOT layer and are collected by the ITO electrode.

We first investigated the effect of additives on light absorption and crystallization of the CH₃NH₃PbI₃ film through UV-vis spectra and X-ray diffraction (XRD). All the films for absorption and XRD measurements were prepared under the same conditions except the difference of additives in perovskite precursor solution (in DMF). The film thickness is around 140–150 nm. As shown in Fig. 2a, all films show absorption onsets at *ca.* 780 nm. Films prepared using CH₃NH₃Cl and NH₄Cl additives exhibit an absorption peak at *ca.* 360 nm and a shoulder at *ca.* 476 nm. The shape of the UV-vis spectra is similar to the reported results.¹³ The film prepared using the NH₄Cl additive shows stronger absorption at 310–500 nm than the film prepared using the CH₃NH₃Cl additive. The film prepared using no additive shows red shift, which might be due to the poor crystallization of CH₃NH₃PbI₃ in the thick film.¹⁹ The XRD peak positions for all CH₃NH₃PbI₃ films on PEDOT:PSS coated glass substrates are nearly the same (Fig. 2b). The diffraction peaks of the CH₃NH₃PbI₃ film prepared using the NH₄Cl additive at 14.28°, 28.62° and 43.42° can be assigned to (110), (220) and (330)

planes, respectively. The diffraction intensities for CH₃NH₃PbI₃ films prepared using different additives are quite different. The inset in Fig. 2b shows the peaks at 14.28°. The diffraction intensity of the CH₃NH₃PbI₃ film prepared using the NH₄Cl additive is much stronger than that of the film prepared using the CH₃NH₃Cl additive. The diffraction peaks of the film prepared using no additive are very weak, suggesting that the additives favor CH₃NH₃PbI₃ crystallization and NH₄Cl is more effective. Strong diffraction peaks for a thin CH₃NH₃PbI₃ film (150 nm) prepared using the NH₄Cl additive indicate that CH₃NH₃PbI₃ is highly crystalline. The size of the nanocrystals in CH₃NH₃PbI₃ films is *ca.* 40 nm, which was calculated from the peak width of the XRD pattern. The XRD patterns for CH₃NH₃Cl and NH₄Cl films can be found in Fig. S1†. The diffraction peaks of CH₃NH₃Cl and NH₄Cl cannot be found in XRD patterns of CH₃NH₃PbI₃ films prepared using the additives, so there is no CH₃NH₃Cl or NH₄Cl crystal in CH₃NH₃PbI₃ films. The effect of annealing time on CH₃NH₃PbI₃ crystallization was studied. The diffraction intensity for the CH₃NH₃PbI₃ film prepared using no additive does not change with annealing time (Fig. S2†). However, the diffraction intensity of the CH₃NH₃PbI₃ film prepared using the NH₄Cl additive increases significantly after being annealed at 100 °C for 30 s. Then XRD patterns remain nearly unchanged, indicating that CH₃NH₃PbI₃ crystallization accomplishes (Fig. S3†).

Perovskite film morphology and surface coverage are crucial to the performance of planar heterojunction perovskite solar cells.¹⁷ So we investigated the morphology of CH₃NH₃PbI₃ films prepared using different additives by scanning electron microscopy (SEM) and atomic force microscopy (AFM). CH₃NH₃PbI₃ films were prepared on PEDOT:PSS coated ITO substrates *via* spin-coating perovskite precursor solution and heating at 100 °C for 30 s. Fig. 3 shows SEM and AFM images of CH₃NH₃PbI₃ films prepared using different additives. The SEM image of the film prepared using no additive exhibited large voids and extremely rough surface. The larger scale image is shown in Fig. S4,† a fiber-like solid and voids in the film can be seen clearly. Nearly no voids can be seen in the film prepared using the CH₃NH₃Cl additive. Pebble-like nanocrystals (70–200 nm) are distributed in the film. The film prepared using the NH₄Cl additive contains uniform nanocrystals (Fig. 3c) and shows better coverage than the film prepared using the CH₃NH₃Cl additive (Fig. S4†). The film prepared using no additive exhibited a root-mean-square (RMS) roughness of 47.5 nm. Films prepared using CH₃NH₃Cl and NH₄Cl additives are much smoother, showing RMS roughnesses of 15.3 nm and 5.2 nm, respectively. The RMS roughness for the film prepared using the NH₄Cl additive is even smaller than that of the best perovskite film reported previously.¹⁶ AFM phase images are consistent with SEM images. Comparing the phase images of the three films, we observe that the films prepared using additives show small and uniform domains, providing a smooth perovskite surface for forming a high-quality PC₆₁BM layer.

Solar cells with structure ITO/PEDOT:PSS/CH₃NH₃PbI₃/PC₆₁BM/Al were fabricated to investigate the effect of additives on photovoltaic performance. Device performance data are listed in Table 1. The device fabricated using no additive exhibited

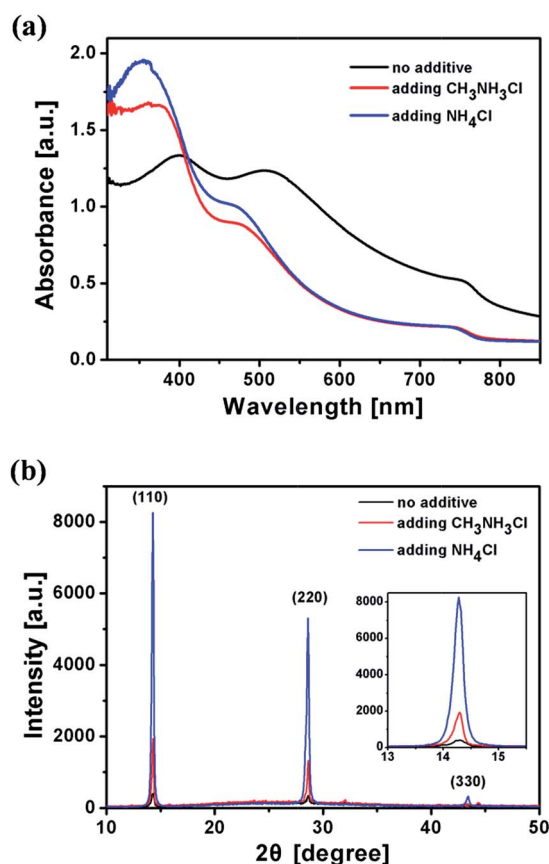


Fig. 2 UV-vis absorption spectra (a) and XRD patterns (b) for CH₃NH₃PbI₃ films fabricated by using different additives.



Fig. 3 SEM (left), AFM height (middle) and phase (right) images for $\text{CH}_3\text{NH}_3\text{PbI}_3$ films fabricated using no additive (a), 17.5 mg mL^{-1} $\text{CH}_3\text{NH}_3\text{Cl}$ (b), and 17.5 mg mL^{-1} NH_4Cl (c), respectively.

Table 1 Performance data for $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells

| Additive | V_{oc} [V] | J_{sc} [mA cm^{-2}] | FF [%] | PCE (average ^a) [%] |
|-----------------------------------|--------------|----------------------------------|--------|---------------------------------|
| Without | 0.37 | 0.36 | 27.53 | 0.04 (0.03) |
| $\text{CH}_3\text{NH}_3\text{Cl}$ | 0.92 | 12.78 | 69.40 | 8.16 (7.97) |
| NH_4Cl | 0.88 | 14.08 | 80.11 | 9.93 (9.75) |

^a Average PCE of 20 devices.

an open-circuit voltage (V_{oc}) of 0.37 V, a short-circuit current density (J_{sc}) of 0.36 mA cm^{-2} , a fill factor of 27.53% and a power conversion efficiency (PCE) of 0.04% (Fig. 4). The performance of the device fabricated using no additive being inconsistent with previous reports^{13,16} is due to the thickness difference between $\text{CH}_3\text{NH}_3\text{PbI}_3$ films. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ film fabricated in this work using no additive is thicker (*ca.* 150 nm), and the imperfect crystallinity and morphology lead to poor device performance. Thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with high crystallinity and good morphology are obtained by using additives, and they give higher J_{sc} than previous films.^{13,16} The optimization data for device performance are listed in Tables S1–S5.† The optimized concentrations of $\text{CH}_3\text{NH}_3\text{Cl}$ and NH_4Cl additives are 20.0 mg mL^{-1} and 17.5 mg mL^{-1} , respectively. The device fabricated using the $\text{CH}_3\text{NH}_3\text{Cl}$ additive gave a V_{oc} of 0.92 V, a J_{sc} of 12.78 mA cm^{-2} , a FF of 69.40% and a PCE of 8.16%. The device fabricated using the NH_4Cl additive gave a V_{oc} of 0.88 V, a J_{sc} of 14.08 mA cm^{-2} , a FF of 80.11% and a PCE of 9.93%. Higher J_{sc}



Fig. 4 J - V curves (a) and EQE spectra (b) for $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells fabricated by using different additives.

and FF of devices fabricated using the NH_4Cl additive result from a highly crystalline, more uniform and smoother $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. The thickness of the PC_{61}BM layer was optimized (Table S3†). A 32 nm PC_{61}BM layer gave the best performance. A thinner PC_{61}BM layer can reduce the series resistance (R_s) of devices, leading to higher FF. The FF decreased when further reducing the thickness of the PC_{61}BM layer, which resulted from the decrease of the shunt resistance. The solar cells fabricated using additives showed high reproducibility, which benefits from high crystallinity and good morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. The integrated photocurrent for the devices fabricated using $\text{CH}_3\text{NH}_3\text{Cl}$ and NH_4Cl additives is 12.26 mA cm^{-2} and 13.32 mA cm^{-2} , respectively, which is consistent with J_{sc} values obtained from J - V measurements. The mechanism how NH_4Cl makes the perovskite film smooth is not clear, possibly related to crystallization kinetics. NH_4Cl could slow down the crystallization process to make perfect perovskite crystals. Good crystallinity and morphology for the perovskite layer favor exciton generation and charge carrier transport. Also, using a high-quality perovskite film, the above electron-transport layer can be made thinner to reduce the series resistance.

In summary, an innovative approach by using the chloride additive to enhance the performance of perovskite solar cells was developed. The effects of two additives $\text{CH}_3\text{NH}_3\text{Cl}$ and

NH₄Cl on perovskite film properties and photovoltaic performance were investigated. Perovskite films fabricated using the NH₄Cl additive are highly crystalline and possess excellent morphology, leading to remarkable enhancement in the device performance. CH₃NH₃PbI₃/PC₆₁BM solar cells fabricated using the NH₄Cl additive gave a decent PCE of 9.93% and a very outstanding FF of 80.11%. Application of this innovative approach in other device structures is ongoing in our lab.

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