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Effective solvent-additive enhanced crystallization and coverage of absorber layers for high efficiency formamidinium perovskite solar cells

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The high efficiency of planar-type perovskite solar cells severely requires good crystallization and high surface coverage for absorber films. However, the two key factors are still main challenges in perovskite films formation to date. Here, the 1-Chloronaphthalene (CN) is used as solvent-additive into the precursor $HC(NH_2)_2PbI_3$ ($FAPbI_3$) solution to control the crystallization and surface coverage of the $FAPbI_3$ films by adjusting its concentration. The CN chlorinated monodentate ligand is likely to temporarily chelate with Pb^{2+} during crystal growth, facilitating homogenous nucleation to form relative high quality $FAPbI_3$ films. Meanwhile, the CN additive with high boiling point delays the growth rate of $FAPbI_3$ film to help form homogenous continuous $FAPbI_3$ films with fewer pin-holes. As a result, with the addition of CN solvent-additive, the efficiency of $FAPbI_3$ planar-type solar cells is enhanced to 16.53%.

The organic-inorganic hybrid perovskite material has emerged as a very effective light absorber material for high efficiency solar cells with its power conversion efficiency (PCE) rapidly risen from 3.8% to 21.0% in just a few years.[1-10]Even for the flexible lightweight cells, efficiency has been improved to 15.4%.[11]The excellent performance is originated from its splendid properties such as high charge carrier mobility, extremely low trap state density, long electron-hole diffusion length, and small exciton-binding energy.[12-15]As morphology of the perovskite films plays a key role in the cell performance, there have been extensive studies in developing high quality films. For example, solvent additives have been frequently used to improve the crystallinity, surface coverage and surface roughness.[16-19]Im et al. used hydrobromic acid (HBr) to grow perovskite film with remarkably improved density.[20]Grätzel et al. attained smoother, highly crystalline and continuous perovskite films by simply adding H_2O in the precursor solution.[21]Snaith et al. utilized hydroiodic acid (HI) as an additive to grow a compact and uniform perovskite film.[22] Jen et al. employed 1, 8-diiodooctane (DIO) as an additive to obtain high quality films.[23] Ma et al. used 1-chloronaphthalene (CN) additive in $MAPbI_{3-x}Cl_x$ perovskite solar cells to fabricate more homogenous perovskite films.[24]

So far most studies are focused on the $CH_3NH_3PbI_3$ ($MAPbI_3$) absorber materials. Another active area of research is to optimize the active layer to expand its absorption spectrum to longer wavelength since the absorption onset of the most popular perovskite $MAPbI_3$ goes only to ~800 nm with most of the near infrared wasted,[25]In this regard, formamidinium ($HC(NH_2)_2PbI_3$, $FAPbI_3$) has been developed as a more effective absorber, [26-28] with narrower band gap ~1.47 eV comparing to 1.55 eV for the $MAPbI_3$. More importantly, materials and processes have been developed to solve the stability problem.[29-32]

In this work, we report an effective process that improves both crystalline quality and surface coverage of the $FAPbI_3$ film using a simple one-step solution technique. We found that the CN with chlorinated ligand chelates with Pb^{2+} in the precursor. The chelation encourages homogenous nucleation to form better quality $FAPbI_3$ film with fewer pin-holes. Meanwhile, the higher boiling point of the CN compound moderates the growth rate of $FAPbI_3$ to form continuous film with better uniformity. The PCE is increased by 15% compared to the cells without the CN additive, with average PCE improved to 15.54% over large area and the champion PCE reached16.53%. We attribute the improved performance to the better crystallization and higher surface coverage.

The planar-type solar cells based on the $FAPbI_3$ active layer were fabricated with the device structure illustrated in **Figure 1a**. The FTO transparent electrode is used as the bottom cathode; the TiO_2 prepared on top of it as the electron transport layer, the spiro-OMeTAD film applied as the HTL; and gold coating as the top anode. The $FAPbI_3$ films were deposited using one-step solution-process. **Figure 1b** shows the cross-sectional SEM image of a completed device. It is clear that the $FAPbI_3$ absorber film is prepared with well-defined crystal grains across the film thickness (~560 nm).

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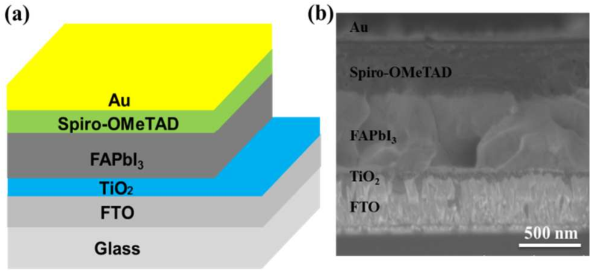

Figure 1 (a) Device architecture of $FAPbI_3$ planar-type solar cell. (b) Representative cross-sectional SEM view of a completed device.

A series of solar cell devices were fabricated using the $FAPbI_3$ precursor solution prepared with CN solvent with different additive concentration. **Figure 2a** displays the J-V curves of the $FAPbI_3$ cells, with key J-V parameters, including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and PCE, summarized in **Table 1**. It appears that the PCE improves first and then decreases with increased CN ratio. The control device fabricated using the pristine $FAPbI_3$ solution without additive exhibits the relatively lower PCE 14.33%, with J_{sc} = 20.39 mA cm^{-2}, V_{oc} = 0.98 V and FF = 0.72. Interestingly, when 1% CN added into the $FAPbI_3$ solution, the J_{sc} is increased to 23.84 mA cm^{-2}, V_{oc} to 1.04 V, FF to 0.67, and PCE to 16.53%. The IPCE curve of the champion device based on 1% CN is shown in **Figure S1**. The calculated J_{sc} value from the IPCE is up to 22.32mA cm^{-2}, in excellent agreement with the direct J-V measurements. When the CN concentration is further increased to 2-3%, PCE of the solar cells are dropped to 12.81% and 9.01%, respectively. It is apparent that the optimized CN additive ratio is 1%. Comparing to the reference solar cell prepared without additive, the cell efficiency is increased by 15%. For reliable measurement, we have studied the J-V characteristics of the champion device using both reverse and forward scan directions, as shown in **Figure S2**. It is believed that the hysteresis is originated from the defects and ions migration within the $FAPbI_3$ film. The defects could act as traps for electrons and holes under forward bias working conditions, and the charges directly fill the traps when the forward scanning, that leads to the poor operation until the traps are filled to the full. Meanwhile, ions migration in perovskite produces the internal capacitance. These reasons generate the J-V hysteresis in $FAPbI_3$ solar cells.[11, 33, 34]To further confirm that the cell fabrication is reproducible, we have prepared 10 individual devices from five different batch runs using the same 1% CN solvent-additive and coating processes. **Figure 2b**shows PCE distribution histograms, with statistics of the J-V measurements listed in **Table S1**. It is clear that all key J-V parameters show very small deviation, demonstrating that the high efficiency solar cell fabrication process is reproducible. Meanwhile, the stability of the device without and with 1% CN additive is measured under AM 1.5G illumination at room temperature for 210 minutes, and the results are shown in **Figure 2c**. It is clear that the device based on CN additive exhibits more stable than the cell without CN. The good stability likely causes the improved crystallization and less pin-holes, as will be discussed later.

It is well known that the surface coverage of the absorber layer has a great influence on the device performance because the low surface coverage would lead to direct electrical contact between the HTL and the ETL, resulting in carrier recombination.[35, 36]The $FAPbI_3$ film prepared from the pristine precursor solution without CN additive shows inferior surface coverage, as shown in **Figure 3a**, leading to poor cell performance. **Figure 3b, 3c** and **3d** shows top-view SEM images of the $FAPbI_3$ films prepared using different CN ratios. It is clear that when the CN solvent-additive added into the precursor solution, the $FAPbI_3$ films show better surface coverage.

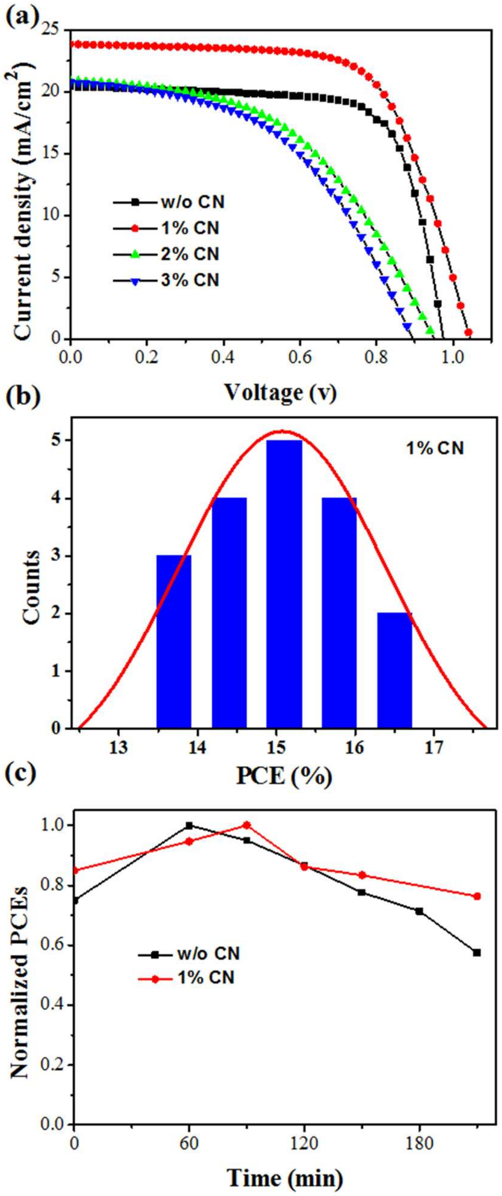

Figure 2 (a) J-V curves of the $FAPbI_3$ solar cells based on various ratio of the CN. (b) The PCE distribution histogram of the $FAPbI_3$ planar-type cells with 1% CN. (c) Normalized PCE as a function of aging time for the $FAPbI_3$ solar cells without CN and with 1% CN solution-additive.

Table1. The parameters of the $FAPbI_3$ planar-type devices with different ratio of CN.

Sample	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE(%)
0 %	0.98	20.39	0.72	14.33%
1 %	1.04	23.84	0.67	16.53%
2 %	0.98	20.83	0.63	12.81%
3 %	0.90	20.76	0.48	9.01%

Figure S3 shows AFM height images of the $FAPbI_3$ films coated with different CN ratios. It is clear that the higher the CN ratio, the better the surface coverage. The root-mean-square (RMS) surface roughness of the $FAPbI_3$ films without CN is 12.9 nm. When the CN solvent-additive is increased to 1%, 2% and 3%, the RMS roughness is increased to 14.0, 15.0 and 16.4 nm respectively. **Figure 3e** exhibits the absorbance spectra of the $FAPbI_3$ films prepared using different CN ratios. The samples with the CN additive show significantly higher absorbance in the short-wavelength spectrum from 400 to 810 nm, indicating fewer pinholes in the $FAPbI_3$ films,[37] in agreement with the SEM results.

The improvement in surface coverage is likely due to the chelation between the CN and PbI_2. **Figure 3f** shows a schematic diagram for the PbI_2-CN chelation. We speculate that the chlorine ligands in the CN chelate with Pb^{2+} ions.[38]During the crystal growth step,[23]it moderates the $FAPbI_3$ crystallization before it is evaporated during the high temperature annealing. As a result, $FAPbI_3$ films are formed with better crystallization and better surface coverage, as shown in **Figure 3b, 3c** and **3d**.

However, **Figure 2a** and **Table 1** show that the solar cell performance is reduced when the CN is increased beyond 1%, even though better surface coverage is achieved using higher CN concentration. In order to get better insight into the fundamental mechanism, XRD were carried out for the $FAPbI_3$ films deposited using different CN ratios. **Figure 4a** shows the XRD patterns of the $FAPbI_3$ films using different CN concentration while other deposition parameters were fixed. All samples display diffraction peaks centered at 14.2°, 19.9°, 24.3°, 28.4°, 31.7°, 34.7°, 40.5°, and 42.7°, corresponding to the (111), (120), (021), (222), (231), (030), (240) and (333) lattice planes, respectively, in good agreement with the previous reports on $FAPbI_3$.[39] Detailed analyses reveal that the film prepared using 1% CN gives the highest peak intensity, demonstrating the best improved crystallization. However, when the CN ratio is increased beyond 1%, the samples show lower peak intensity. As better crystallinity improves charge diffusion lengthand transport kinetics,[40]the cells prepared using 1% CN show the highest PCE (16.45%) with J_{sc} of 23.84 mA cm^{-2} and large V_{oc} of 1.04 V. The high J_{sc} is originated from the high crystallization of $FAPbI_3$ films. It is worthwhile to note that the high V_{oc} (1.04 V) achieved is likely due to smaller potential loss for photoexciton dissociation[23]as the band gap for the $FAPbI_3$ is only about 1.5 eV, as estimated from **Figure 3e**.

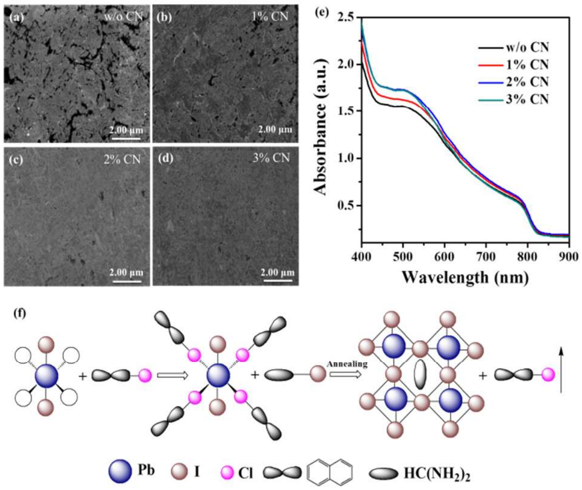

Figure 3 Top-view SEM images of $FAPbI_3$ film without CN solvent-additive (a), and with 1% CN solvent-additive (b), 2% CN solvent-additive (c), 3% CN solvent-additive (d). (e) Absorbance spectra of the $FAPbI_3$ films with different ratio of the CN. (f) Schematic diagram for the chelation of PbI_2 and CN.

We have measured the steady state photoluminescence (PL) to study the charge transfer and recombination loss.[11]**Figure 4b** shows the steady-state PL spectra of the $FAPbI_3$ films prepared using different CN ratios. It is clear that the $FAPbI_3$ film prepared using the pristine precursor solution without the CN additive shows the highest PL intensity, indicating that there is serious recombination in the film. Meanwhile, the PL intensity decreases as the CN ratio increases, demonstrating that the charge transfer effectively occurred before the carrier recombination. We have prepared the $FAPbI_3$ films with and without CN, and tested their PL decay time by time resolved-PL. **Figure 4c** displays the TRPL spectra of $FAPbI_3$ films with different CN ratios. The key TRPL parameters are listed in **Table S2**. For the pristine $FAPbI_3$ film, the average PL decay time is 77.29 ns. Interestingly, the average PL decay time increases with enhanced CN ratios. The long decay time is essential for long exciton diffusion length, which is beneficial to improving the device. However, the $FAPbI_3$ solar cells show poorer performance when the CN concentration is increased to above 1%. We attribute it to inferior crystallization (**Figure 4a**). However, the $FAPbI_3$ solar cells show poorer performance when the CN concentration is increased over 1%. This phenomenon is accredited to inferior crystallization (**Figure 4a**). Compared to the control devices prepared from the pristine $FAPb_3I$ precursor, the 1% CN ratio significantly improved surface coverage, crystallization, and reduced charge recombination, resulting in increased J_{sc} and V_{oc} for the $FAPbI_3$ solar cells.

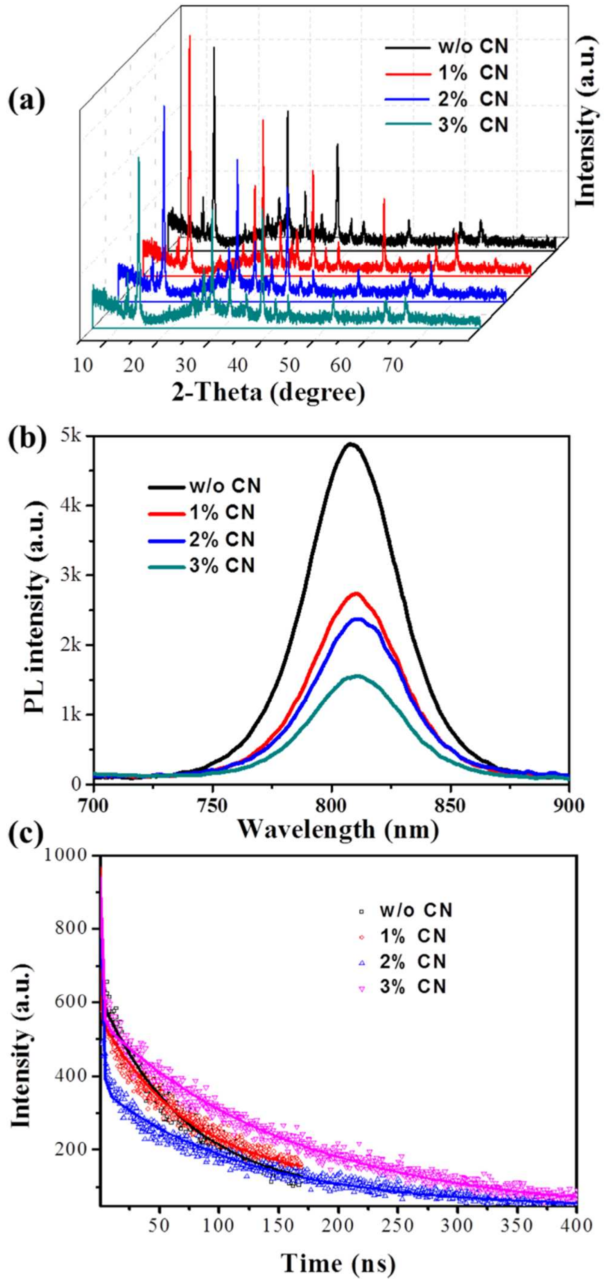

Figure 4 (a) XRD spectra of the $FAPbI_3$ films with various ratio of CN. (b) Steady state PL spectra of the $FAPbI_3$ films with different ratio of CN using an excitation wavelength 532 nm irradiated. (c) TRPL spectra of the $FAPbI_3$ films with different CN ratios.

In summary, we demonstrated that the CN is an efficient solvent-additive to improve performance of the $FAPbI_3$ solar cells. The chlorinated ligand in CN likely chelate with Pb^{2+} during crystal growth to moderate the thin film formation, leading to higher crystallization and more surface coverage of the absorber layer. Compared to the control device fabricated using the pristine $FAPbI_3$ precursor solution, the efficiency is enhanced by 15%, from 14.33% to 16.53%. The good crystallization and higher surface coverage effectively improve the charge transport and suppress charge recombination, resulting in improved and V_{oc} in solar cells.

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