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Effect of 4-tert-butylpyridine on Perovskite Formation and Performance of Solution-Processed Perovskite Solar Cells

Yantao Shi,*a Xiangyuan Wang,a Hong Zhang,a Bo Li,a Huilan Lu,a Tingli Ma,b Ce Haoa

To obtain highly efficient perovskite solar cells (PSCs), effective controls on perovskite crystallinity, homogeneity, and surface morphology are crucial. Herein, we demonstrate the flexible and facile use of TBP to improve the crystallinity of perovskite in two-step or one-step route. For the two-step route, addition of TBP into DMF when dissolving PbI₂ for spin-coating resulted in a porous layer composed of randomly packed PbI₂ nanocrystals. This approach subsequently offered a widely enlarged contact area to facilitate interfacial reaction with CH₃NH₃I and greatly improved CH₃NH₃PbI₃ crystallization. Based on this strategy, the PCEs of the CH₃NH₃PbI₃-based PSCs were improved from 6.71% to 10.62% (i.e., 58% enhancement). For one-step route, TBP as an additive resulted in orientational and better crystallinity, by which the PCEs of CH₃NH₃PbI₃·Cl-based planar PSCs increased from 11.11% to 15.01%, showing a remarkable enhancement of as high as 35%. Using TBP as one multifunctional additive, it is thought that our strategy in this work offers a new idea for fabrication of highly efficient PSCs.

1. Introduction

In the past three years, organometal halide perovskites have been considered extraordinary photovoltaic materials with desirable properties, such as moderate direct band-gap, high carrier mobility, ambipolar behaviour in charge transport, and facile solution processability. For thin-film solar cells, organometal halide perovskites are not only good photoabsorbers, but also superior charge transport media (for both electrons and holes), which facilitate high photoelectric conversion efficiencies (PCEs) and provide more flexibility in cell architecture design. High PCEs from 9.7% in 2012 to 20.1% in 2015 have been achieved successively by perovskite solar cells (PSCs) with either mesoporous or planar architectures. To obtain highly efficient PSCs, effective controls on perovskite crystallinity, homogeneity, and surface morphology are crucial. High-quality perovskite can be prepared by vapor-assisted methods. However, solution routes are more advantageous and competitive for large-scale production. In recent years, various efforts have been exerted to upgrade solution routes and photovoltaic performances of corresponding PSCs have been improved largely.

Initially, we prepared perovskite by depositing a mixture of two precursors (i.e., PbI₂ and CH₃NH₃I) in a single step onto mesoporous TiO₂ films. However, the uncontrolled precipitation process in this method usually results in large morphological variations, wide distribution in photovoltaic performance, and poor reproducibility. In 2013, disadvantages of one-step method were remedied by introducing sequential deposition method that was conducted by initially depositing mesoporous TiO₂ with PbI₂; subsequently, these materials were dipped into CH₃NH₃I solution. For solution routes, at the early stage, this method largely progressed from “one-step” to “two-step”, by which high PCEs of up to 15% were achieved in 2013. Nevertheless, the two-step route is unsuitable for fabrication of all kinds of PSCs, such as planar ones. Successful use of the “two-step” route mainly depends on the mesoporous scaffolds that can offer large surface area to enable sufficient contact of PbI₂ with CH₃NH₃I for perovskite formation. However, for planar PSC fabrication, the contact between two precursors usually is very limited. Thus, the PbI₂ layer, especially the part that is distant from the contact interface, cannot be fully converted into perovskite.

Recent studies revealed that the use of specific additives and solvents is extremely effective for improving perovskite crystallization and PSC performance, especially for planar PSCs fabricated via the one-step or two-step routes. Various specific processing methods were developed based on different additives, and some mechanisms were proposed accordingly. A modified two-step method is conducted by dissolving PbI₂...
Scheme 1. Schematic diagram of the “two-step” route in which a porous and free-standing PbI$_2$ film is used to react with CH$_3$NH$_3$I to obtain highly crystallized CH$_3$NH$_3$PbI$_3$ perovskite.

with dimethylsulfoxide instead of N,N-dimethylmethanamide (DMF). By employing this strategy, problems of incomplete conversion and uncontrolled particle sizes of perovskites were largely alleviated in the absence of mesoporous scaffold, thereby increasing film reproducibility and planar PSC. By contrast, for planar PSC fabrication by one-step routes, the additives are significant in facilitating homogeneous nucleation or crystallization kinetics modulation. Currently, highly uniform and pinhole-free perovskite films, such as CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbI$_3$Cl$_x$, and HC(NH$_2$)$_3$PbI$_3$ have been prepared with the use of some additives, such as 1,8-diiodooctane, N-cyclohexyl-2-pyrrolidione, HI, and NH$_3$Cl.  

4-Tert-butylpyridine (TBP) is a commonly used additive in electrolytes of dye-sensitized solar cells and in hole transport materials of PSCs. In the present report, we demonstrate the flexible and facile use of TBP to improve the crystallinity of perovskite in two-step or one-step route. For the two-step route, addition of TBP into DMF when dissolving PbI$_2$ for spin-coating resulted in a porous layer that was constructed by randomly packing PbI$_2$ nanocrystals. This approach subsequently offered a widely enlarged contact area to facilitate interfacial reaction with CH$_3$NH$_3$I and greatly improved CH$_3$NH$_3$PbI$_3$ crystallization, as shown in Scheme 1. Based on this strategy, the PCEs of the CH$_3$NH$_3$PbI$_3$-based PSCs were improved from 6.71% to 10.62% (i.e., 58% enhancement). For one-step route, TBP as an additive resulted in orientational and better crystallization, by which the PCEs of CH$_3$NH$_3$PbI$_3$Cl$_x$-based planar PSCs increased from 11.11% to 15.01%, showing a remarkable enhancement of as high as 35%.

2. Experimental section

PSCs Fabrication. Typically, FTO glass (15 Ω sq$^{-1}$) was patterned by etching with Zn powder (6–9 μm, Alfa Aesar, 97.5%) and hydrochloric acid (HCl, 4 M, Sigma-Aldrich), then followed by consecutive cleanings with 2% hexamethane solution (Sigma-Aldrich, being diluted into working concentration as received), deionized water, acetone and isopropanol, and finished through drying samples in clean air. Compact TiO$_2$ blocking layer (C-TiO$_2$) was fabricated by spin coating organic sol on the clean substrates at 3000 rpm for 30 s, followed by sintering in a furnace at 450°C in air for 2 h. Organic sol for TiO$_2$ compact layer was prepared according to previous literature. CH$_3$NH$_3$PbI$_3$-based PSCs were fabricated through the route of two-step sequential deposition. To prepare PbI$_2$ film for the normal sample, the first step 462 mg PbI$_2$ (Sigma-Aldrich, 99.999%) was dissolved into 1 mL anhydrous dimethyl formamide (DMF, J&K, anhydrous, 99.8%) and then were spin-coated on C-TiO$_2$/FTO substrate at 5000 rpm for 10 s, finally drying at 70°C for 30 min in glove box. Preparation of the porous PbI$_2$ film for sample 2-TBP-guided-ST was conducted by adding 80 μL 4-tert-butylypyridine (TBP, J&K, 96%) into above PbI$_2$ solution (as that for sample 1-Normal-TS) and then treated with the same procedures mentioned above. After cooling to room temperature, the PbI$_2$ films were dipped into a solution containing 10 mg CH$_3$NH$_3$I in 1 mL 2-propanol (IPA, J&K, anhydrous, 99.5%) for 2 min, then rinsed with 2-propanol and dried at 70°C for 30 min to form the crystallized CH$_3$NH$_3$PbI$_3$. Above two CH$_3$NH$_3$PbI$_3$ samples are named as 1-Normal-TS and 2-TBP-guided-TS, respectively, where TS refers to the “two-step” method, and 1 or 2 is the sample number. For fabrication of CH$_3$NH$_3$PbI$_3$Cl$_x$ normal film, one precursor solution was firstly prepared by adding 102.2 mg PbCl$_2$ (Sigma-Aldrich, 99.999%) and 174.9 mg CH$_3$NH$_3$I (with a molar ratio of 1:3) into 500 μL anhydrous DMF and then heated at 70°C for 1 h. This sample is named as 3-Normal-OS, where “OS” represents one-step method. For sample 4-TBP-guided-OS, 40 μL TBP was added into above precursor solution additionally. CH$_3$NH$_3$PbI$_3$Cl$_x$ films were fabricated by spin-coating of precursor solution at 2000 rpm for 30 s. The coated films were then placed on a hot plate set at 90°C for 1h and 100°C for 25 min. The HTM (hole transport material) prepared by dissolving 72.3 mg spiro-MeOTAD (Borun Company, China, 98%), 28.8 μl TBP, and 20 μl solution of 300 mg ml$^{-1}$ Co(III) TFSI salt [Co(PyPz)$_2$][TFSI], MaterWin Technology, >99%) in acetonitrile, and 17.5 μl solution of 520 mg ml$^{-1}$ lithium bis(trifluoromethylsulphonyl)imide (LiTFSI, Sigma-Aldrich, 99.95%) in acetonitrile (J&K, 99.8%) into 1 mL chlorobenzene (Alfa Aesar, 99.5%) was deposited by spin coating at 3000 rpm for 30 s. Finally, the fabrication of PSCs was completed after depositing 100 nm Ag (Alfa Aesar, 99.9%) by means of thermally evaporation on top of the HTM layer. The active area of this electrode was fixed at 0.12 cm$^2$.

Characterizations: Microscopic morphology and crystallinity were characterized by scanning electron microscopy (SEM, FEI Quanta 450) and X-ray diffraction (XRD, D/Max-2400, Rigaku, Japan), respectively. The UV-Vis absorbance spectra of perovskite were measured with a UV-Vis spectrophotometer (HP 8453, Hewlett Packard, USA) by deducting the background of the compact TiO$_2$ layer. Photocurrent-voltage ($I$-$V$) curves were measured under AM 1.5, 100mW cm$^{-2}$ irradiation (PEC-L15, Peccell, Yokohama, Japan) by a Keithley digital source meter (Keithley 2601, USA). Before each $I$-$V$ measurement, the light intensity was calibrated with a standard crystalline silicon solar cell. IPCE measurements were performed using a monochromatic light from a system made of a xenon lamp, a monochromator, and appropriate filters.
3. Results and discussion

As shown in Figures 1a and 1b, a relatively compact PbI$_2$ film approximately 100 nm in thickness was obtained through the normal route. After the reaction with CH$_3$NH$_3$I solution, larger and closely packed CH$_3$NH$_3$PbI$_3$ crystals were formed in sample 1-normal-TS with sizes ranging from 200 nm to 500 nm, as shown in Figures 1c and 1d. For TBP-guiding, we obtained a free-standing and porous PbI$_2$ film composed of randomly packed nanoparticles, as illustrated in Figures 1e and 1f. The porous PbI$_2$ film is more advantageous compared to the compact one because a greatly enlarged surface area is available for the subsequent reaction with CH$_3$NH$_3$I solution.

Figure 1. SEM images of PbI$_2$ film and CH$_3$NH$_3$PbI$_3$ films. (a) and (b): compact PbI$_2$ film prepared without TBP-guiding; (c) and (d): CH$_3$NH$_3$PbI$_3$ film (sample 1-Normal-TS) prepared using the compact PbI$_2$ film; (e) and (f): porous PbI$_2$ film prepared by TBP-guiding; (g) and (h): CH$_3$NH$_3$PbI$_3$ film (sample 2-TBP-guided-TS) prepared using the porous PbI$_2$ film.

Figure 2. (a) XRD patterns of PbI$_2$ films; (b) transmittance spectra of PbI$_2$ films; (c) XRD patterns of CH$_3$NH$_3$PbI$_3$ films, the insert are the extracted part; (d) UV-Vis absorbance spectra of CH$_3$NH$_3$PbI$_3$ films, the insert are digital photos of the cells.
which is necessary for full conversion of PbI$_2$ into CH$_3$NH$_3$PbI$_3$.

Although the mechanism by which TBP guided the formation of PbI$_2$ nanoparticles in the present work is unclear, we believe that the “guiding” effect of TBP is highly relevant to the coordination effect between Pb$^{2+}$ and TBP. Compared with the oxygen atom on DMF, the nitrogen atom on TBP (pyridine nitrogen) as electron-donating unit is more inclined to coordinate with Pb$^{2+}$. We conjecture that such greater coordination can eventually tune PbI$_2$ crystallization into nanosized particles. In addition, TBP can also act as dispersing agent (similar to some surfactants) that is capable of hindering the formation of large-sized bulks or aggregates. Based on the porous PbI$_2$, the morphology of the resultant CH$_3$NH$_3$PbI$_3$ film for sample 2-TBP-guided-TS is very different from 1-normal-TS as this material is also porous. In addition, this material has numerous large hollow pores with diameters exceeding 100 nm. The CH$_3$NH$_3$PbI$_3$ crystals were also found to interconnect well around the pores. This condition is an important prerequisite for efficient carrier transport. To the best of our knowledge, the present study proposed a tuning method or a morphology that has never been reported.

The crystallinities of PbI$_2$ films prepared using the normal and TBP-guided, two-step routes were characterized by X-ray diffraction (XRD), as shown in Figure 2a. Furthermore, to probe the evolution of crystallinity of PbI$_2$ before and after heating, one fresh film (drying in air, without baking) and one baked at 70 °C for 30 min were measured. Detailed assignments of the diffraction peaks for each curve in Figure 2a are demonstrated in Figure S1. For the PbI$_2$ sample prepared without TBP guiding, all diffraction peaks in either the fresh film or the one baked at 70 °C for 30 min correspond well to PbI$_2$, suggesting no formation of crystallized PbI$_2$-DMF complex. On the other hand, the PbI$_2$ crystallization in the case of using only DMF as solution is highly oriented. This result is consistent with that reported previously.$^{10}$ By contrast, based on the strong and strange diffraction peaks (marked with “#”) observed in the fresh film with TBP guiding, it is evident that PbI$_2$-TBP complex has been formed. Even after baking at 70 °C for 30 min, peaks (at 2θ = 22.8° and 28.1°) that belong to PbI$_2$-TBP complex also exist. XRD results indicate that TBP and PbI$_2$ have strong interaction, under which a intermediate (one complex) can be formed in the preparation of PbI$_2$ film. In light transmittance measurement from 500 nm to 800 nm, the porous PbI$_2$ film allows the transmission of above 80% incident light, as illustrated in Figure 2b. By contrast, only a small fraction of incident light can go through the compact PbI$_2$ film. This characterization actually reflects the nature of these two films, namely, compact and porous. Figure 2c shows XRD patterns of the resultant CH$_3$NH$_3$PbI$_3$ films prepared according to the two different two-step routes. In 1-normal-TS sample, a substantial portion of PbI$_2$ was apparently not converted into CH$_3$NH$_3$PbI$_3$ because the characteristic peak intensity for PbI$_2$ (001) plane is still very strong. By contrast, in 2-TBP-guided TS sample, the diffraction peak for PbI$_2$ is relatively very weak, as clearly illustrated by the comparison in the inset of Figure 2c. This finding also suggests that our TBP-guided route is very facile and effective. For the normal two-step route, such problem may be resolved through reaction time alteration. However, extending the dipping time in CH$_3$NH$_3$I solution is not feasible because this process will result in the formation of extremely large crystals (several microns), which hinder electron transport through perovskite film and deteriorate charge recombination.$^{10}$ As shown in Figure 2d, 2-TBP-guided TS samples shows relatively high absorbance in the whole visible and some near-infrared light regions because of good crystallinity. By comparison, the PSC based on 2-TBP-guided TS is darker than the one based on 1-normal-TS, as illustrated in the inset of Figure 2d. By high resolution mass spectrometry (HRMS), we confirmed that TBP has been fully.

![Figure 3](image-url)
curves of the PSCs; (c) Distribution diagrams of power conversion efficiencies (PCEs) from CH$_3$NH$_3$PbI$_3$-based PSCs.

**Table 1.** Detailed photovoltaic parameters of the PSCs fabricated by two-step route.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scan mode</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$FF$ (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Normal-TS</td>
<td>Reverse scan</td>
<td>0.83 ± 0.06</td>
<td>8.05 ± 5.68</td>
<td>0.37 ± 0.06</td>
<td>2.55 ± 2.07</td>
</tr>
<tr>
<td></td>
<td>Reverse scan</td>
<td>0.92</td>
<td>17.12</td>
<td>0.43</td>
<td>6.71</td>
</tr>
<tr>
<td></td>
<td>Forward scan</td>
<td>0.88</td>
<td>17.32</td>
<td>0.26</td>
<td>3.88</td>
</tr>
<tr>
<td>2-TBP-guided-TS</td>
<td>Reverse scan</td>
<td>0.90 ± 0.04</td>
<td>19.58 ± 1.00</td>
<td>0.49 ± 0.04</td>
<td>8.66 ± 0.82</td>
</tr>
<tr>
<td></td>
<td>Reverse scan</td>
<td>0.96</td>
<td>21.27</td>
<td>0.52</td>
<td>10.62</td>
</tr>
<tr>
<td></td>
<td>Forward scan</td>
<td>0.92</td>
<td>22.50</td>
<td>0.34</td>
<td>7.06</td>
</tr>
</tbody>
</table>

removed after the formation of TBP-guided perovskite film (see Figure S2 and S3 in supporting information).

Figure 3a illustrates the J–V curves of the champion devices based on the PSCs fabricated via the two different two-step routes; the J–V curves were measured under AM 1.5 and 100 mW cm$^{-2}$ simulated light. Detailed photovoltaic parameters including that of the champion devices and the mean values of 35 devices for each group are summarized in Table 1. For 1-normal-TS-based PSCs, the mean PCE is extremely low, which is only 2.55% (Table 1). Low short-circuit current density ($J_{sc}$) and fill factor ($FF$) are specifically responsible for the unsatisfactory results. Previous studies reported that in some conditions, residual PbI$_2$ in perovskite was advantageous to PSC performance. This outcome was caused by the finding that proper amount (usually very small) of PbI$_2$ is favorable in the suppression charge-recombination at the TiO$_2$/perovskite interface or grain boundaries of perovskite crystals. Meanwhile, in 1-normal-TS sample, the amount of residual PbI$_2$ was relatively large (as confirmed by XRD results mentioned above); therefore, transport and collection of photo-generated electrons would be affected seriously. Consequently, we can obtain neither large $J_{sc}$ nor $FF$ because the residual PbI$_2$ will directly result in the increase in series resistance ($R_s$) and deterioration in charge-recombination. For 1-normal-TS-based PSCs, another serious problem is the poor reproducibility. Table 1 also shows that the $J_{sc}$ value shows an extremely large distribution, which further confirms the poor controllability when using the normal two-step route. As demonstrated in Figure 3a, the champion device for 1-normal-TS-based PSCs exhibits a PCE of only 6.71%, whereas the one based on 2-TBP-guided-TS route provide a relatively higher PCE of 10.62%, which was greatly enhanced by 58%. All photovoltaic parameters have been found to improve for 2-TBP-guided-TS-based PSCs, wherein $J_{sc}$ and $FF$ contributed most to the final PCE. Apparently, the enhancement in photovoltaic performance was derived from the improved CH$_3$NH$_3$PbI$_3$ crystallinity. In PSCs, the hysteresis phenomenon is very common, which has generally been attributed to the migration of ions within the perovskite film or to the transient ferroelectric polarization. Improving the crystallinity of the perovskite films has proved effective in term of eliminating the hysteresis phenomenon. Although hysteresis still exists in 2-TBP-guided-TS-based PSCs, it has been alleviated a lot when compared to the one prepared by the normal route. Obviously, the amelioration in hysteresis was achieved as a result of the improved crystallinity of perovskite by TBP-guiding. Spectra of the monochromatic incident photon-to-electron conversion efficiency (IPCE) are shown in Figure 3b. From 300 nm to nearly 800 nm, 2-TBP-guided-TS-based device was more efficient than 1-normal-TS-based device and exceeds 80% in the region from 355 nm to 560 nm. Moreover, based on this modified two-step route, the reproducibility has also improved greatly, as shown in Figure 3c. In 2013, Snaith proposed three probable future directions for PSC technology, including the “porous perovskite p-n heterojunction” architecture, which is similar to the bulk heterojunction organic solar cells. Compared to planar p-i-n cell architecture, the “porous p-n heterojunction” may benefit from the enlarged interfacial contact between perovskite and charge-selective material, which is favorable to the extraction of photogenerated carriers. However, no report still has been published regarding such PSCs. Therefore, our research study may provide one important idea for fabrication of “porous perovskite p-n heterojunction” PSCs.

For one-step routes, additives are very effective in promoting homogeneous crystallization of high-quality perovskite films for planar p-i-n junction PSCs. In the present work, the abovementioned results motivated us to use TBP in
Regardless of the chemical components, PbCl₂ is used as precursor in preparing CH₃NH₃PbI₃₋ₓClₓ films. We also introduced TBP into the CH₃NH₃PbI₃₋ₓClₓ synthesis via the one-step route. Details of the synthesis can be found in the Experimental section. The 3-normal-OS samples were prepared by the normal one-step route. This CH₃NH₃PbI₃₋ₓClₓ film was condensed using numerous pinholes, as illustrated in Figures 4a and 4b. In addition, we can hardly find any isolated and distinguishable crystals as observed in CH₃NH₃PbI₃ samples because of the fused grain boundaries. Similar to other additives, initial TBP was expected to be able to promote homogeneous nucleation and result in high-quality CH₃NH₃PbI₃₋ₓClₓ film. However, the 4-TBP-guided-OS sample we obtained using this strategy was not a pinhole-free film, as shown in Figures 4c and 4d. However, at least two different crystallization forms can be found in Figure 4c. Similar to sample 3-normal-OS, the first form exhibits smooth surface and large scale. Meanwhile, the second crystallization form is composed of large quasi-cuboid-like crystals that are formed from the first crystallization, which are approximately hundreds and tens of nanometers in length and width, respectively. We infer that the formation of these crystals is

Figure 5. (a) XRD patterns of CH₃NH₃PbI₃₋ₓClₓ films; (b) UV-Vis absorbance spectra of CH₃NH₃PbI₃₋ₓClₓ films; (c) J-V curves of CH₃NH₃PbI₃₋ₓClₓ-based PSCs; (d) IPCE curves of CH₃NH₃PbI₃₋ₓClₓ-based PSCs; (e) Distribution diagrams of PCEs of CH₃NH₃PbI₃₋ₓClₓ-based PSCs.
due to the preferred orientation of crystals caused by TBP. Finally, it is confirmed that TBP has been fully removed after the formation of TBP-guided CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ film (see Figure S4). The XRD patterns in Figure 5a indicate that, compared to sample 3-normal-OS, the crystallization of sample 4-TBP-guided-OS shows preferred orientation along (110) direction as the evident increases for diffraction intensities of (110) and (220) planes are observed when compared with (310) or (211). Usually, the difference in the crystallinity for perovskite film may lead to the change in properties. For example, the two samples show different UV-vis absorbance. Figure 5b shows that TBP-guided perovskite film prevails the normal sample in the whole range from 400 nm to 800 nm, which possibly has been caused by better crystallinity when compared to the normal sample (3-Normal-OS). A total of 35 cells were examined for each sample. The average and highest performances are summarized in Table 2.

Table 2. Detailed photovoltaic parameters of the PSCs fabricated by one-step route.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scan mode</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Normal-OS</td>
<td>Reverse scan</td>
<td>0.82 ± 0.05</td>
<td>19.94 ± 2.28</td>
<td>0.61 ± 0.06</td>
<td>9.86 ± 0.94</td>
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<tr>
<td></td>
<td>Reverse scan</td>
<td>0.82</td>
<td>22.47</td>
<td>0.61</td>
<td>11.11</td>
</tr>
<tr>
<td></td>
<td>Forward scan</td>
<td>0.76</td>
<td>22.43</td>
<td>0.52</td>
<td>8.74</td>
</tr>
<tr>
<td>4-TBP-guided-OS</td>
<td>Reverse scan</td>
<td>0.90 ± 0.06</td>
<td>21.62 ± 1.98</td>
<td>0.65 ± 0.06</td>
<td>12.64 ± 1.40</td>
</tr>
<tr>
<td></td>
<td>Reverse scan</td>
<td>1.04</td>
<td>21.09</td>
<td>0.69</td>
<td>15.01</td>
</tr>
<tr>
<td></td>
<td>Forward scan</td>
<td>0.98</td>
<td>20.81</td>
<td>0.64</td>
<td>12.96</td>
</tr>
</tbody>
</table>

Conclusions

In summary, we demonstrated a novel strategy for tuning perovskite crystallization in PSCs by a flexible and facile method involving the use of TBP in one-step and two-step routes. For two-step routes, porous PbI$_2$ could be constructed, which then offered an extremely enlarged contact area to facilitate interfacial reaction with CH$_3$NH$_3$I and greatly improved CH$_3$NH$_3$PbI$_3$ crystallization. Based on this strategy, the highest PCEs of the CH$_3$NH$_3$PbI$_3$-based PSCs were improved from 6.71% to 10.62% (i.e., 58% enhancement). Furthermore, TBP was also used as effectively as additive for a one-step route in fabricating CH$_3$NH$_3$PbI$_3$-Cl$_X$-based planar PSCs. The use of TBP resulted in an overall higher crystallinity. This feature plays a positive role in increasing the photovoltage of materials. Finally, the PCE of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$-based PSCs exhibited a remarkable enhancement of up to 35% (i.e., from 11.11% to 15.01%).

Acknowledgements

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Notes and references


Facile use of TBP generated notable improvement on perovskite crystallinity and photovoltaic performance of perovskite solar cells.