Tailoring perovskite compounds for broadband light absorption

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Abstract. Perovskite solar cells have experienced an outstanding advance in power conversion efficiency (PCE) by optimizing the perovskite layer morphology, composition, interfaces, and charge collection efficiency. To enhance PCE, the mixed perovskites were proposed in recent years. In this study, optoelectronic performance of pure perovskites and mixed ones were investigated. It was demonstrated that the mixed perovskites exhibit superior to the pure ones. The mixed material can absorb broadband light absorption and result in increased short circuit current density and power conversion efficiency.

1. Introduction

Since the pioneering work of Snaith's group\(^1\), who demonstrated a simple planar heterojunction solar cell, planar perovskite devices have been receiving great attention due to the simplicity in processing\(^2\). A lot of work was conducted including perovskite compound engineering, hole and electronic transfer material engineering, interface engineering, and device structure engineering. Thanks to past efforts, an efficiency of up to 22.1% for perovskite solar cell was reached in 2016\(^3\), superior to their organic rivals and comparable to silicon solar cell.

It has already showed that chemical modification of cations\(^4\) and anions\(^5\) in perovskite materials can tune the bandgaps. For example, substitution of the anion I with Br in MAPbI\(_3\) (MA= methylammonium) results in the bandgap variation from 1.5 eV to 2.3 eV. On the other hand, HC(NH\(_2\))\(_2\)PbI\(_3\), which contains formamidinium (FA) cations instead of MA cations in the perovskite structure, has a bandgap of 1.48 eV, with an absorption edge of 840 nm. MA-based lead iodide (MAPbI\(_3\)) perovskite materials possess a band gap of 1.57 eV. A strategy for extending the absorption range of solar light is thus to replace MAPbI\(_3\) with FAPbI\(_3\). Replacing the MA cation with the FA cation, which has an ionic radius relatively larger than that of MA\(^+\) in the organic-inorganic lead iodide perovskite material, can change the metal-halide-metal bond angle and thus leads to a narrower band gap compared to that of MAPbI\(_3\). However, FAPbI\(_3\) has two crystal structures\(^5\), i.e., a trigonal structure (perovskite phase, black color, \(α\)-FAPbI\(_3\)) and a hexagonal structure (nonperovskite phase, yellow color, \(δ\)-FAPbI\(_3\)), depending on the synthesis temperature. The \(α\)-FAPbI\(_3\) is stable at a high temperature (over 160 °C) and can convert into \(δ\)-FAPbI\(_3\) under an ambient humid atmosphere. To prevent the transformation of \(α\)-FAPbI\(_3\) to \(δ\)-FAPbI\(_3\), preparation of \((\text{FAPbI}_3)_{1-x}(\text{MAPbI}_3)_x\), which is a more stable new perovskite, was regarded as an effective route.

Here, a comparison of optoelectronic performance between pure and mixed perovskites were reported, including morphology and absorption spectrum as well as the device performances of different perovskite solar cells.
2. Experimental Section

2.1 Synthesis of the inorganic–organic mixed perovskite
Methylammonium iodide (CH3NH3I) and formamidinium iodide (NH2CH5NH2I) were synthesized according to the reported procedure7,8 by reacting the hydroiodic acid (10 mL, 57 wt % in water, Sigma-Aldrich) and methylamine and mormamid (24 mL, 33 wt % in absolute ethanol, Sigma-Aldrich) at 0 °C with stirring for 60 min. Raw CH3NH3I and NH2CH5NH2I were obtained by removing the solvent at 50 °C on a rotary evaporator. The material was then washed in diethyl ether and filtered several times. The precipitate was then dried in vacuum oven overnight at 50 °C and then kept in nitrogen-filled glovebox.

The perovskite solution was prepared by mixing 1.2 mmol of PbI2 (or PbBr2) (99.99%, Alfa Aesar) and 1.2 mmol of CH3NH3I (or NH2CH5NH2I) in 1 mL of anhydrous N,N-dimethylformamide (DMF, Sigma-Aldrich). To prepare perovskite films, 50 μL of perovskite precursor solutions was spin coated onto the substrates at 5000 rpm for 55 s. During the spin-coating, 50 μL of anhydrous chlorobenzene (Sigma-Aldrich) was quickly dropped in the center of the substrates after six or seven seconds. The spin-coated films were transferred onto a hot plate for drying at 100 °C for 2 min and then annealed under different atmospheres at 100 °C for 30 min. The desired solutions of MAPbI3, FAPbI3, MAPbBr3, FAPbBr3, (FAPbI3)1-x(MAPbI3)x, and (FAPbBr3)1-x(MAPbBr3)x were prepared.

2.2 Device fabrication
Solar cells with ITO/PEDOT:PSS/perovskite/PCBM/Ag planar device structure were prepared. The ITO glass substrates (1.5 cm × 1.5 cm) were ultrasonically cleaned with detergent, deionized water, acetone, and ethanol, sequentially, and then were blow-dried in nitrogen. Before deposition of other films, the ITO substrates were treated with ultraviolet-ozone for 10 min. After that, PEDOT:PSS solution (Clevious Al 4083) was spin-coated on ITO-coated substrates at 3000 rpm for 45 s, and subsequently the PEDOT:PSS films were annealed at 150 °C for 20 min. After perovskite films were deposited, 20 mg/mL of PCBM (FEM. Inc.) solution in chlorobenzene was then spin-coated at 1000 rpm for 45 s. Finally, Ag top contact was deposited by evaporation through an aperture mask under a base pressure of 7 × 10-6 Torr. The active device area is 0.12 cm².

2.3 Measurement and characterization
Scanning electron microscope (SEM) images were obtained using Hitachi S5200. Atomic force microscopy (AFM) measurements were performed using Asylum Research MFP-3D. Current–voltage measurements were carried out using Keithley 2400 at room temperature under AM 1.5G illuminations (1000 W/m²) from a solar simulator, which was calibrated using a standard silicon solar cell device.

3. Results and discussions

3.1 Morphology of perovskite films
The mixing ratio x was optimized by conducting a series of contrastive experiments. It was found that the performance of mixed perovskites can reach highest at x=0.15, which agrees well with the reported4. Therefore, (FAPbBr3)0.15(MAPbBr3)0.85 and (FAPbI3)0.15(MAPbI3)0.85 were prepared for comparison here. Figure 1 shows the morphology of as-prepared perovskite films on ITO glass. It is found that the perovskites with Br anions have large surface roughness, which can be seen from Figure 1(a),(c),(e). It is interesting that the perovskites with FA cations can produce small roughness. The maximum height of surface roughness on FA perovskites is no more than 70nm, as compared to that one of over 200nm on MA perovskites. In experiments it was oberserved that MA crystalline perovskites with large grain size are easily formed. Therefore, addition of FA perovskites is also beneficial to smooth the device surface, which results in better performance. It is worth pointing out that the rough surface can be made much smoother by post washing or vapour annealing methods5.
3.2 Absorption spectrum of perovskite films

Figure 2 presents the absorption spectrum of the perovskite films on ITO glass. For the perovskites with Br anions, it is obvious that the perovskite films show a small absorption edge of about 550nm, corresponding to a band gap of 1.8eV, which agrees well with the reported results in ref.[6]. For the mixed perovskite of (FAPbBr$_3$)$_{0.15}$(MAPbBr$_3$)$_{0.85}$, the absorption behaves worse than that of pure MAPbBr$_3$ but better than that of FAPbBr$_3$. The reason for such low absorption for Br based perovskites is that its large band gap blocks most of the light, which surface shows yellow transparency(Figure 3a). For example, MAPbBr$_3$ has a band gap of about 2.3eV. Therefore, it is very important for high efficiency solar cells to choose the mixing ratio in (FAPbBr$_3$)$_{x}$(MAPbBr$_3$)$_{1-x}$.

The perovskites with I anions show an absorption edge of about 800nm. As compared to pure perovskites, the mixed ones enhance all the light absorption from 500nm to 1100nm wavelengths. Even in the wavelength range of 800nm to 1100nm the perovskites are not sensitive to, the light absorptions improve greatly. At 900nm, the absorption is enhanced by 3 times and 15 times compared with FAPbI$_3$ and MAPbI$_3$, respectively.

![Figure 1. AFM images of (a) MAPbI$_3$, (b) FAPbI$_3$, (c) MAPbBr$_3$, (d) FAPbBr$_3$, (e) (MAPbBr$_3$)$_{0.85}$(FAPbBr$_3$)$_{0.15}$, and (f) (MAPbI$_3$)$_{0.85}$(FAPbI$_3$)$_{0.15}$](image1)

![Figure 2. UV-VIS absorption spectrum of all the samples](image2)
Figure 3. The as-prepared perovskites on ITO glass. (a) MAPbBr₃; (b) From left to right: MAPbI₃, FAPbI₃, (MAPbI₃)₀.₈₅(FAPbI₃)₀.₁₅

3.3 Cell performances
Figures 4a shows the cross-sectional SEM image of a completed ITO/ PEDOT:PSS/ (MAPbI₃)₀.₈₅(FAPbI₃)₀.₁₅ / PCBM /Au planar solar cell. Each layer could be clearly defined according to the contrast variation of the cross-sectional image. It can be seen that the mixed perovskites are porous. This is because we didn’t use any post-treatments, such as non-polar solvent washing, thermal annealing, solvent annealing, and so on. Figure 4b shows the current density-voltage (J-V) curves for these cells. The photovoltaic parameters are also summarized in Table 1. The devices with MAPbBr₃, FAPbI₃, FAPbBr₃ present small open circuit voltages (Vₒc) below 800mV, small short circuit current densities (Jₛc) below 2.5 mA/cm² and a fill factor (FF) of 50%-60%, leading to very low PCEs of no more than 1.1%. As a result, the cell based on the mixed perovskite of (MAPbBr₃)₀.₁₅(FAPbBr₃)₀.₈₅ is naturally deserved with a low PCE. But it is obvious that the cell performance of the mixed perovskites is superior to those with pure materials, which should be attributed to different band gaps of both perovskite materials. For MAPbI₃, the performance is improved with a Vₒc of 853.57mV and a Jₛc of 9.42 mA/cm² although with a relatively low FF of 50.54, and its efficiency increases to 4.06%. When mixing the material with FAPbI₃, the Vₒc, Jₛc, and FF are all improved and thus PCE continue to increase up to 6.55%, which also accords well to the absorption spectrum illustrated in Figure 2. It was reported that a longer charge diffusion length and superior stability in FAPbI₃ films compared to those in MAPbI₃. Although our experiments didn’t demonstrate this point clearly, MAPbI₃ and FAPbI₃ mixed perovskites definitely pose a broadband light absorption and consequently deliver a greater efficiency.

Figure 4. (a) Cross-sectional SEM image of a completed ITO/ PEDOT:PSS/ (MAPbI₃)₀.₈₅(FAPbI₃)₀.₁₅ / PCBM /Au planar solar cell. (b) J–V curves of planar perovskite solar cells with different device structures.
Table 1. Photovoltaic parameters from (MAPbI$_3$)$_{0.85}$(FAPbI$_3$)$_{0.15}$.

| Perovskites | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE(%) |
|-------------|--------------|----------------------|----|--------|
| MAPbI$_3$   | 853.57       | 9.42                 | 50.54 | 4.06   |
| FAPbI$_3$   | 746.5        | 1.76                 | 53.04 | 0.70   |
| MAPbBr$_3$  | 784.52       | 2.3                  | 60.16 | 1.08   |
| FAPbBr$_3$  | 705.09       | 0.15                 | 52.99 | 0.06   |
| (MAPbBr$_3$)$_{0.15}$(FAPbBr$_3$)$_{0.85}$ | 862.04 | 2.48 | 68.93 | 1.47 |
| (MAPbI$_3$)$_{0.15}$(FAPbI$_3$)$_{0.85}$ | 831.71 | 12.66 | 62.21 | 6.55 |

4. Conclusions
The mixed perovskite of (MAPbI$_3$)$_{0.85}$(FAPbI$_3$)$_{0.15}$ for broadband light absorption have been described. The mixed perovskite of (MAPbI$_3$)$_{0.85}$(FAPbI$_3$)$_{0.15}$ delivers higher performance than pure materials such as MAPbI$_3$, FAPbI$_3$, MAPbBr$_3$, FAPbBr$_3$, and even than other mixed material of (MAPbBr$_3$)$_{0.15}$(FAPbBr$_3$)$_{0.85}$. This mixing strategy may lead to more efficient and cost-effective inorganic-organic hybrid perovskite solar cells.

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