

Control the crystal size by varying concentrations of precursors for the planar perovskite solar cells

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ABSTRACT: The influence of the grain size of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ on the solar cell performance is investigated by controlling the ratio between $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 precursors. As the concentration of the precursors increased from 1.0M to 2.0M, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ grain size increased from ~100nm to ~400nm. The solar cell utilizing the $\text{CH}_3\text{NH}_3\text{PbI}_3$ with large grain size shows improved photocurrent compared to the solar cell utilizing $\text{CH}_3\text{NH}_3\text{PbI}_3$ with small grain size, which is ascribed to the reduced recombination at the boundaries of grains.

Organic-inorganic halide perovskite solar cells (PSCs) utilizing $\text{CH}_3\text{NH}_3\text{PbI}_3$ photoactive layer have attracted considerable attention in recent years owing to their advantages such as low cost, light weight and ease of fabrication[1-4]. Perovskite solar cells have been considered as the most viable option for the next generation photovoltaics; there has been a rapid progress in the field of PSCs and the power conversion efficiencies (PCE) have been improved from ~3% to ~20% [5-7]. There are three primary types of perovskite solar cell structures. The first type involves $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer deposited on a mesoporous metal oxide layer(TiO_2 , Al_2O_3)[8, 9].

The second type utilizes $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer prepared by sequential vapor-phase deposition of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 precursors. The third type is the planar heterojunction perovskite solar cell consisting of conducting polymer/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ / fullerene structure, which is similar to the organic photovoltaic architecture. Compared to the first and second type perovskite solar cells, the planar heterojunction solar cells (type three) benefit from the ease of solution process and low processing temperature under 100 °C. Herein, we investigated the effect of the grain size of perovskite on the performance of perovskite solar cell by adjusting the precursor concentrations. We found that the grain size of perovskite plays an important role on the perovskite crystal

size and that it can be controlled by the precursor concentration.

Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was synthesized using the method described by Michael M. Lee, et al. (Ref). Lead (II) iodide PbI_2 (99.999%, ultra dry) was purchased from Alfa Aesar. The indium thin oxide (ITO) substrates were cleaned and the poly (3,4-ethylenedioxythiophene) poly (styrenesulphonate) (PEDDOT:PSS) layer was spin coated on the ITO as hole transport layer. $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were dissolved in anhydrous γ -butyrolactone (GBL) and dimethyl sulfoxide DMSO (7:3 molar ratio) at different concentrations ranging from 1M, 1.5M and 2.0M. The perovskite films were annealed at 100 °C for 60 minutes. The mixture solutions were spin coated onto PEDDOT:PSS layer with a two consecutive step method. (1000rpm, 10s. 7000rpm 60s) On the second step, the anti-solvent chlorobenzene (CB) 1ml was dropped after 15 seconds of the spin-coating process. The perovskite films were annealed at 100 °C for 60min. After the formation of the perovskite films, [6,6]-phenyl-C61-butyric acid methyl ester PCBM dissolved in CB with a concentration of 15mg/ml was spin coated onto the perovskite films. The devices were completed by the thermal evaporation of 0.5nm Lithium fluoride and 100nm aluminum electrode.

The current-voltage (I-V) curves of the devices were measured using a Keithley 2400 Source Measure Unit. The simulator (McScience K201 LAB50) used was an AM 1.5G from Oriol. UV-visible absorption spectra were obtained by UV-2450 (SHIMADZU, Japan). Field emission scanning electron microscope (FE-SEM) images were obtained using JSM-6700F (JEOL, Japan).

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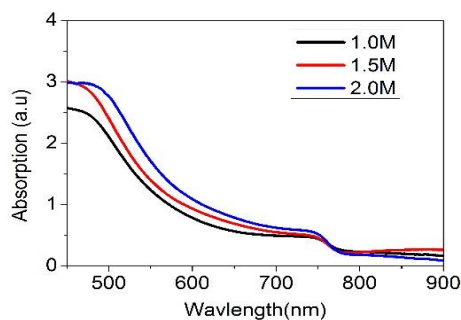


Figure 1. UV-vis absorption spectra of perovskite film prepared from 1.0, 1.5 and 2.0M precursor solution, respectively.

The absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared with varying molar ratios are shown in Fig 1. The absorption of the perovskite films from 450nm to 800nm indicated the strong photon light harvesting capability. As shown in the Fig 1, the intensity of absorption gradually increased as the concentration of precursor ratio increased from 1.0M to 2.0M. The film thicknesses were 350nm, 380nm and 420nm, respectively. This indicated that the thicker film can be easily achieved by tuning the concentration of precursor ratio. The thicker film prepared at 2.0M precursor solution was able to absorb more photons compared to the thinner films prepared from 1.0M and 1.5M precursor solutions.

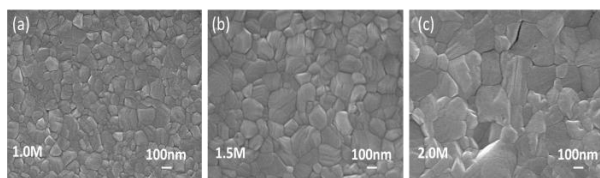


Figure 2. SEM images of (a) 1.0M perovskite film, (b) 1.5M perovskite film and (c) 2.0M perovskite film

To gain a better insight into perovskite crystallization processed by different precursor concentration, the SEM measurement was conducted. It is well known that the perovskite film morphology is critical for the highly efficient perovskite devices. As seen in the Figure 2, all of the perovskite films fully covered the substrate, and when the precursor ratio was increased the grain size grew as well. As a conclusion, the concentration of the perovskite had positive correlation to the perovskite grain size. By increasing the concentration of precursor solutions, the viscosities of the solutions could be increased, which reduced the wetting properties of the perovskite film. The larger grains yielded less grain boundaries, indicating the close packing of the perovskite grains. This characteristic may have led to improved charge transport properties for photovoltaic devices.

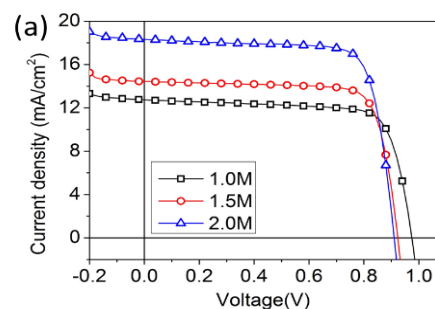


Figure 3. (a) J-V curves and (b) EQE spectra of 1.0, 1.5, 2.0M perovskite solar cells.

Table 1. Parameters for devices processed from 1.0, 1.5M, 2.0M precursor solutions of perovskite solar cells.

Device	J_{sc} mA/cm ²	V_{oc} V	FF %	Eff %
1.0M	12.7	0.97	76.2	9.4
1.5M	14.5	0.92	78.4	10.4
2.0M	18.3	0.91	79.5	13.2

The current density-voltage (J)-(V) characterization of the perovskite film solar cells prepared by different precursor concentrations was shown in fig 3 (a). The PSCs prepared from 1.0M had a PCE of 9.5%. The maximum improvement in PCE was obtained when the precursor concentration was increased from 1.0M to 2.0M. In this case, the PCE value increased from 9.5% to 12.9%, corresponding to a 35% improvement. This improvement in PCE was primarily due to the 44% enhancement in J_{sc} which increased from 12.7 to 18.3 mA cm⁻², as shown in figure 3 and table 1. By incorporating the SEM image analysis, the significant increase in crystal size can explain the dramatic increase in J_{sc} . Thus, we believe that the reduced grain boundaries, which could act as the traps leading to the charge recombination, is the reason behind the enhancement of the perovskite devices. The large grain size also resulted in the slight enhancement of the FF by enhancing the charge transport in the crystals.

In Summary, the efficient planar heterojunction perovskite solar cells were successfully fabricated by adjusting the concentration of the precursor. The large $\text{CH}_3\text{NH}_3\text{PbI}_3$ grains with size about 400 nm were obtained from the 2.0 M precursor solution. Increasing the precursor concentration increased viscosities of the solution and reduced wettability of the solution, which turns out to be advantageous to the growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystals.

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REFERENCES AND NOTES

1. Aldibaja, F.K., et al., Effect of different lead precursors on perovskite solar cell performance and stability. *J. Mater. Chem. A*, **2015**. 3(17): p. 9194-9200.
2. Bai, Y., et al., High performance inverted structure perovskite solar cells based on a PCBM:polystyrene blend electron transport layer. *J. Mater. Chem. A*, **2015**. 3(17): p. 9098-9102.
3. Gong, X., et al., Controllable Perovskite Crystallization by Water Additive for High-Performance Solar Cells. *Advanced Functional Materials*, **2015**. 25(42): p. 6671-6678.
4. Stranks, S.D. and H.J. Snaith, Metal-halide perovskites for photovoltaic and light-emitting devices. *Nat Nanotechnol*, **2015**. 10(5): p. 391-402.
5. Luo, S. and W.A. Daoud, Recent progress in organic-inorganic halide perovskite solar cells: mechanisms and material design. *J. Mater. Chem. A*, **2015**. 3(17): p. 8992-9010.
6. Niu, G., X. Guo, and L. Wang, Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A*, **2015**. 3(17): p. 8970-8980.
7. Song, T.-B., et al., Perovskite solar cells: film formation and properties. *J. Mater. Chem. A*, **2015**. 3(17): p. 9032-9050.
8. Wang, F., et al., HPbI₃: A New Precursor Compound for Highly Efficient Solution-Processed Perovskite Solar Cells. *Advanced Functional Materials*, **2015**. 25(7): p. 1120-1126.
9. He, M., et al., High efficiency perovskite solar cells: from complex nanostructure to planar heterojunction. *Journal of Materials Chemistry A*, **2014**. 2(17): p. 5994-6003.