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Research paper

Evolution of the precursor solution and effect on morphology of perovskite film

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HIGHLIGHTS

- Aging of the precursor solution containing PbI_2 and CH_3NH_3I resulted in fast crystallization rate of perovskite film.
- Aging of the precursor solution resulted in a more uniform perovskite film.
- In solution PbI_2 flakes were gradually dissociating into small oligomers, and then form complex with CH_3NH_3I.
- Several hours aging for the precursor solution is suggested.

ABSTRACT

Organolead-halide-perovskite-based solar cells have recently attracted significant attention due to excellent photovoltaic performance and low cost. To improve the conversion efficiency, lots of efforts have been devoted to optimize chemical components and the film fabrication. However, the kinetics of solutes in solution and its effect on the film quality are less understood. Our results reveal that aging of the precursor solution containing PbI_2 and CH_3NH_3I facilitated crystallization and resulted in a more uniform film. Further analysis indicates that in solution PbI_2 flakes were gradually dissociating into small oligomers, and then form complex with CH_3NH_3I.

1. Introduction

Perovskite has been widely investigated as photoactive material used in solar cells, owing to its advantages such as high light-harvesting, low cost and simple fabrication. As we know, the PCE of perovskite-based solar cell has reached 20% till now. Generally, perovskites bear a common chemical formula, i. e. ABX_3, where A is monovalent cation such as $CH_3NH_3^+$, $NH_2CH = NH_2^+$ [1], Cs^+ [2–4], B can be Pb^{2+} or Sn^{2+} [5,6], and X is halide ion I^-, Br^-, Cl^- [3,7]. And also, it can be mixture of the ions listed, particularly in the case of X. Thus great effort has been devoted to optimize the chemical components to improve the conversion efficiency. Beside component, another key factor that affects the device efficiency is the film morphology, which is strongly depended on the fabrication process.

There have been several reports focusing on the evolution of the as-prepared film under thermal treatment [8–10], demonstrating the presence of crystal transition from precursor to perovskite. However, there are few studies on the kinetics of precursor in solution, which is really relative to the feature of the as-obtained film. For example, to improve the uniformity and smoothness of the film, during spin coating another solvent can be casted onto the drying solution by optimizing the crystallization kinetics [11,12]. Hsinhan et al. found that aged precursor solution resulted in a more uniform perovskite film and higher PEC of the solar cell [13], indicating the gradual solutes evolution in solution. Apparently, a process of coordination, nucleation and crystallization are unavoidable during spin coating as for the totally different crystal structures between product and precursors. As known, $CH_3NH_3PbI_3$, a typical perovskite compound, bears a cubic and tetragonal lattice system, where Pb^{2+} is in 6-fold coordination surrounded by an octahedron of I^-, and the $CH_3NH_3^+$ with larger size usually fills in the room built by four adjacent octahedrons. While lead iodide can be looked as a stack of PbI_2 flakes, in which the iodine atoms take a hexagonal close-packed structure with alternating layers of lead atoms, and each lead ion is coordinated by six iodine atoms [14]. The crystal discrepancy implies the unavoidable conformation transfer of the solutes in solution, for example the PbI_2 sheets dispersing into solvent, dissociating into pieces, coordinating with CH_3NH_3I, and then crystallizing into perovskite. These kinetic processes are key factors relative to the film quality and device efficiency, however they are less studied till now. In present work, the formation kinetics of perovskite film with

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typical component of $MaPbI_3$ has been investigated. We found that solutes in DMF did perform complicate phase evolution, which lasts several hours and will influence the film futures.

2. Experimental section

2.1. Perovskite thin-film preparation

CH_3NH_3I (MaI) was synthesized by adding hydroiodic acid (HI) (30.0 ml, ≥45.9 wt%, Sinopharm Chemical Reagent Co., Ltd) into methylamine (CH_3NH_2) (15.0 ml, 40 wt% inaqueous solution, Alfa Aesar) at 0 °C for 2 h with constant stirring under a nitrogen atmosphere. The as-synthesized methylammonium iodide was crystallized through removing the solvent by a rotary evaporator. The generated white powder was washed with diethyl ether (Alfa Aesar) three times and dried under vacuum overnight. To prepare perovskite film, the synthesized MaI and PbI_2 (Aldrich) were solved into DMF resulting in a concentration 0.6 M MaI and 0.3 M PbI_2, and after 1 min ultrasound the solution was spin coated on cover glass at 3000 rpm for 40 s. Here the molar ratio of MaI and PbI_2 are 2:1, and unless additional information provided the concentrations were used. Perovskite film preparation was carried out in a dry nitrogen glove box with humidity < 5%.

2.2. Measurements

The UV–Vis absorption spectra were recorded using a spectrophotometer (SPECORD® 210 PLUS analytik-jena). Resonance light scattering (RLS) were performed on a fluorescence Spectrophotometer (F-4500 HITACHI). X-ray diffraction (XRD) patterns of the films were obtained on an X-ray diffractometer (SmartLab Rigabu). The morphology of the films was characterized by AFM in a tapping mode (Keysignt N9418S 9500). The conductivity of perovskite solution was measured by Conductivity Meter (S230-USP/EP METTLER TOLEDO). A microscope (6XB-PC Shang Guang) has been used to get the optical morphology of the films.

3. Results and discussion

As known, during spin coating a significant color changing from yellow to brown could be seen on the substrate, corresponding to the transformation from precursor solution to perovskite phase. Actually, a careful insight indicated that this process includes two color alternations: from brilliant yellow to colorless and then to brown. They are in responding to the two kinetics processes: solution flowing away from substrate and solvent evaporating from the residual solution [15–17], respectively. Normally, the duration of these processes last over ten seconds, however we found it is different for a fresh precuresor solution and for an aged one, i.e. the color change for the fresh solutions appears sooner. To pursue a systematic study on the solution evolution, a fresh mixture solution of PbI_2 and MaI in DMF was prepared, and then every one hour it was applied to produce film by spin coating. To get the accurate delay time of the color change, processes of the spin coating have been recorded in video (ESI). By checking the videos carefully, we found that the durations of the first stage were closed in all cases, with a constant value of 5 s, within which solution flowing away from the substrate resulted in a liquid film adhering on the surface. During this stage the fade on the substrate should be ascribed to the occurrence of PbI_2-MaI-DMF intermediate as the evaporation of excess DMF [18]. On the other hand, the durations of the second stage are varying, where prolonged aging times resulted in shorter ones. Fig. 1 plots the durations of the second stage as a function of the aging time of the solution. It is reasonable to hypothesize that within the first several hours solutes in solution have been performing an evolution, which finally affected their crystallization kinetics.

To check the effect of formation kinetics on film morphology, optical microscope images of the series of films from different aging time

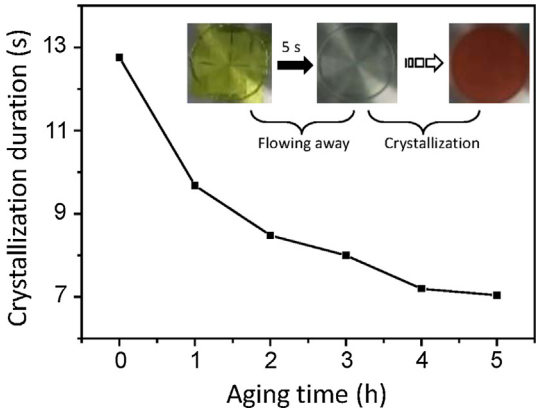

Fig. 1. Dependence of the crystallization duration on the aging time of the DMF solution containing 0.3 M PbI_2 and 0.6 M MaI. The inset shows pictures captured from the video to illustrate the two steps of color changing during spin coating.

solution were taken. From the results (Fig. 2), it is clear that the enhancement of the aging time leads to improved uniform and higher coverage. Furthermore, AFM was employed to characterize the morphology. Fig. 3 displays the cross sectional profiles extracted from AFM images, where to get the film thickness a groove has scratched carefully on the film by using a tip [19]. In agreement with the optical images above, longer aging of the precursor really leads to weaker fluctuated profile curve. In addition, according to the average values of the platform and bottom (marked as red lines over the curves), the average thickness of films could be calculated. Despite various fluctuations, the average thicknesses for all cases are closed, at the level of 250 nm. The similar thickness implies a same amount of solute per unit area in all cases. Since the same concentration of precursor solution, the same amount of solute means that at the end of the first stage the height of liquid films left on substrate should be similar for all cases [14]. Thus the various durations of the second stage is not caused by the solution amount but due to the different crystallization rate of solute, which is essentially dependent on the states of solute molecules. Spencer et al. [20] found that precursor solution after standing for 2 weeks resulted in an improved coverage of the perovskite film in comparison to that without standing, and this was ascribed to the efficient dissolution of $PbCl_2$. Thus it is reasonable to ascribe the phenomenon above to solute dispersion kinetics.

The crystal structures were investigated and Fig. 4 shows the results. Three intense diffraction peaks at 14.19°, 28.49°, and 31.95°, corresponding to the (1 1 0), (2 2 0) and (3 1 0) crystal planes of the tetragonal structure, respectively [21], confirms the formation of perovskite. While the additional peak at 11.43°, which has been assigned to PbI_2 phase [22], indicates the impurity of the film. Here, the PbI_2 peak intensity shows a decrease trend upon the aging time increasing. Considering to the film morphologies above, we anticipate that longer aging leads to less residual PbI_2 phase in solution, and homogenous precursor solution is the premise of uniform film. Kirmayer group [23] has demonstrated the presence of $PbCl_2$ nanoparticles in DMF precursor solution. In spite of the different crystal structure between $PbCl_2$ and PbI_2, the XRD data still support the assumption that PbI_2 have performed a gradual evolution in solution, for example dispersion in solvent and forming complexes.

To understand the kinetics of solute in solution, a series of measurements have been conducted. From the UV–vis absorption spectrum evolution, a little decrease can be observed (Fig. S1 in SI) upon the time increasing. Further, resonance light scattering (RLS) was used to explore the solute dissolution. As shown in Fig. 5, the marked scattering signals of the mixture at 489 nm indicate the presence of particle pieces in solution, and further the similar RLS profiles in PbI_2 indicate that the