Construction of high performance CH₃NH₃PbI₃-based solar cells by hot-casting technique

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ABSTRACT

Two-dimensional plane CH₃NH₃PbI₃ crystals in millimeter size have been first successfully constructed on FTO glass coated with mesoporous TiO₂ by hot-casting technique. Depending on the closely and continuous arrangement of large perovskite crystals in the film, a best power conversion efficiency (PCE) of 16.01% was achieved along with a photocurrent density of 21.32 mA/cm², an open circuit voltage of 1.07 V and a fill factor of 0.70 from the corresponding CH₃NH₃PbI₃-based solar cells with p-i-n structure. Even more exciting was the quite good stability of the hot-casting-based device, which remained at more than 91% under 55% humidity for 10 days.

1. Introduction

Organic-inorganic hybrid perovskite solar cells have attracted considerable attention in recent years because of the numerous desirable properties, which are promising candidate for next generation photovoltaic technology [1–4]. From the beginning of 2014, the power conversion efficiency (PCE) of perovskite solar cells based on CH₃NH₃PbI₃ structure up to higher than 20% has been achieved on both planar and mesoporous structures [5,6]. In order to improve the performance of the device, several technologies have been developed for the preparation of high quality perovskite thin films, such as: one-step spin-coating, two-step sequential solution deposition, vapor-assisted solution process, dual-source vapor deposition in a high-vacuum chamber and so on [7–10]. However, the size of perovskite crystal was usually between tens of nanometers to several microns, so it was easy to form pinholes on the film. This not only caused electrical shorting but also deleteriously impacted charge dissociation/transport/recombination for devices [11–14]. In addition, based on the stability and reliability of the device, planar-hetero-junction perovskite solar cells with mesoporous architecture have been widely recognized in practical research and application [15,16]. Thus, a series of basic problems regarding the device structure and material properties in perovskite-based device have been attracting more and more researchers' interests. Among them, it can be concluded that large crystal size, full coverage and compact aggregation morphology of perovskite films were rather important for high performance perovskite solar cells [17–20].

In this work, two-dimensional CH₃NH₃PbI₃ crystals in millimeter size have been successfully constructed on mesoporous TiO₂ (m-TiO₂) surface by hot-casting methods. By controlling the process conditions, CH₃NH₃PbI₃ crystals were continuous and aggregated closely in the film. A best power conversion efficiency (PCE) of 16.01% was achieved along with a photocurrent density of 21.32 mA/cm², a voltage of 1.07 V and a fill factor of 0.70 from the corresponding CH₃NH₃PbI₃-based solar cells with FTO/block TiO₂/m-TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD structure. The hot-casting process was simple and efficiency. It needed only a few seconds and microliters of precursor solutions in the whole procedure. Excellent stability of the hot-casting-based device has also been detected, the PCE of which remained at more than 91% (from 16.01% to 14.59%) under 55% humidity ambient condition for 10 days, whereas the one prepared by two-step method was decayed from ~12.50% to 1% over 7 days. More important, the large two-dimensional plane CH₃NH₃PbI₃ crystals must be much more meaningful research work in theory and other optoelectronic devices.

2. Experimental

Methylammonium iodide (MAI) was synthesized according to the literature reported in previous [21]. CH₃NH₃I was synthesized in ice bath by adding hydroiodic acid (HI, 57 wt% in water, Sigma-Aldrich) into methylamine (33 wt% in ethanol, Sigma-Aldrich) and stirring for 2 h. The precipitate was washed by dissolving in a minimum amount of ethanol and then adding in a large amount of diethyl ether. The precipitate was collected by filtration. The procedure was repeated

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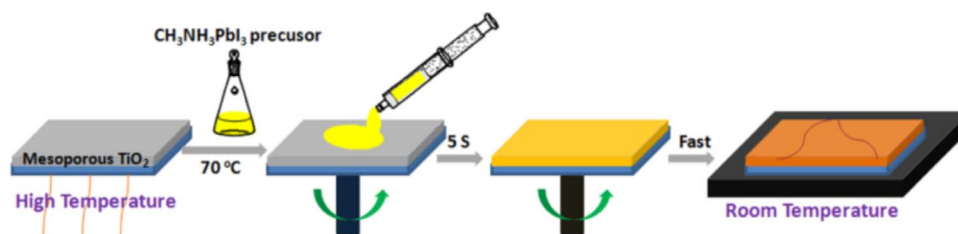
Scheme 1. Processing scheme for $CH_3NH_3PbI_3$-based thin-film on FTO/m-TiO$_2$ layer using hot-casting methods.

three times to get pure MAI. The resulting product (white powder) was dried at 60 °C. The perovskite precursor was prepared by mixing MAI and PbI$_2$ (99%, Sigma-Aldrich) in a molar ratio of 1:1 in anhydrous N. N-dimethylformamide (DMF; 99.99%, Sigma-Aldrich) or γ-butyrolactone (GBL; 99.99%, Sigma-Aldrich), and the final concentration of the perovskite was controlled to approximately 100 mg/mL. FTO substrates were cleaned sequentially with detergent, deionized water, acetone, ethanol, and isopropyl alcohol under ultrasonic for 10 min. TiO$_2$ compact layer was then deposited on the substrates by aerosol spray pyrolysis at 450 °C using a commercial titanium diisopropoxide bis (acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (1:39, volume ratio) as precursor and oxygen as carrier gas. The m-TiO$_2$ layer composed of 20-nm-sized particles was deposited by spin-coating at 5000 rpm for 30 s using a commercial TiO$_2$ paste (Dyesol 18-NRT, Dyesol) diluted in ethanol (2:7, weight ratio). After drying at 125 °C, the TiO$_2$ films were gradually heated to 500 °C, baked at this temperature for 15 min.

As shown in Scheme 1, the FTO substrate was placed on the hot stage for more than ten minutes to ensure that the substrate was heated completely. Then move the substrate onto the prepared spin-coating apparatus suddenly. 80 μL of $CH_3NH_3PbI_3$ precursor solution (100 mg/mL) was dropped to the substrate under the condition of high speed rotating (4000 rpm for 5 s).

After moving the sample to another plate in room temperature in fast speed, the film sample turn reddish brown color in 3 mins because of the formation of large $CH_3NH_3PbI_3$ crystal.

3. Results and discussion

The morphology of m-TiO$_2$ film and $CH_3NH_3PbI_3$ film was characterized by scanning electron microscope (SEM) and polarizing microscope. As shown in Fig. 1A, the SEM image of m-TiO$_2$ films with 20 nm of holes was the same as literature reported. In another, the boiling point of the solution was very important for the formation of large $CH_3NH_3PbI_3$ crystals and high quality film in the process of hot-casting technique. When the $CH_3NH_3PbI_3$ precursor solution was dipped out and contacted with the rotating substrate surface in high temperature, the major solvent in the precursor solution would be volatilized. Large crystals would be formed immediately after the sample was moved onto a room temperature plate in fast speed. Note that $CH_3NH_3PbI_3$ crystals were not only grown toward plane direction and compact accumulation in the film but also could fully fill the hollows of m-TiO$_2$ layer. Accordingly, the specific film morphology in hot-casting technique was attributed to the sudden temperature changes. If the temperature was not high enough, too much solvent would be left on the film after hot spin coating, so the corresponding crystals formed on the film would be not fully and not good enough after left it in room temperature, the microscope photos of which can be seen in Fig. 1A and Fig. 1B. Oppositely, if the temperature was too high, all of the solvent would be volatilized and some crystals formed on the film would be destroyed (as shown in Fig. 1C). So, 175 °C was selected as the proper temperature to fabricate excellent $CH_3NH_3PbI_3$ film for DMF solvent by this technique. After careful observation, it can be seen that the scale of $CH_3NH_3PbI_3$ crystals in the film can reach as high as 0.5 mm. As contrast, the crystal scale of $CH_3NH_3PbI_3$ prepared

on FTO/m-TiO$_2$ substrate by the popular two-step method was less than 500 nm (Fig. 1B). The process of preparing $CH_3NH_3PbI_3$ films by two-step method were described in Supporting Information (SI).

In order to confirm the applicability and regulation of the hot-casting technique further, another typical polar solvent of GBL was also used to repeat the process. Large $CH_3NH_3PbI_3$ crystals were also formed on the film in the same way which can be seen from Fig. 1G–J, but the crystal size was obviously smaller than the one from DMF solvent. That is because the boiling point of GBL is higher than DMF, and $CH_3NH_3PbI_3$ have better solubility in GBL than in DMF, so the crystal is not easy to be separated out suddenly.

It can be concluded that the morphology of $CH_3NH_3PbI_3$ films can be controlled by the growth way of perovskite crystals, which determined the properties of the films. Fermi level of the flat film with full surface coverage on TiO$_2$ was closer to the middle of the band-gap, as compared to the rough perovskite film with partial coverage on TiO$_2$. As literatures reported, the $CH_3NH_3PbI_3$ film with large sized crystal and full surface coverage should have higher light harvesting in the visible spectral range, faster electron extraction rate, and lower defect density, resulting in better photoelectric response in the range of 500–800 nm and higher power conversion efficiency [22].

The samples of hot-casting $CH_3NH_3PbI_3$ film (DMF solution) deposited on FTO substrates coated with m-TiO$_2$ was further characterized by X-ray diffraction (XRD) and the diffraction patterns are shown in Fig. 2a. Obviously, strong diffraction peaks located at 14.1°, 28.5° and 31.8° for 2 h scan are observed corresponding to the planes of (110), (220) and (310), which are rather consistent with previous reports [23,24], so it can be indicated that the tetragonal perovskite structure has been formed. In another, XRD characterization of $CH_3NH_3PbI_3$ prepared using GBL solution was also provided to confirm the crystallization of $CH_3NH_3PbI_3$. As shown in Fig. S1, the diffraction peaks were completely consistent with the sample fabricated by DMF solution, which confirmed that no excess impurities in the perovskite film.

The thickness of $CH_3NH_3PbI_3$ films is important for their devices [25,26], which can be controlled by the speed of spin-coating. Different speeds of spin-coating have been tried on hot substrate in our work, the results have been shown in Fig. 2b. It can be seen that the thickness of perovskite film is decreasing with the speed increasing of spin-coating. 80 μL of $CH_3NH_3PbI_3$ precursor solution (100 mg/mL in DMF) was used to drop on the substrates during the hot-casting process. The thickness of the $CH_3NH_3PbI_3$ film can reach 320 nm under the speed of 4000 rpm/s, and the best quality films with full coverage have been achieved in this condition. According to the literature report, 300–400 nm of active layer was an ideal thickness for high performance perovskite solar cells [27–29]. The thickness of the $CH_3NH_3PbI_3$ layer was measured by section SEM technique, which is shown in Fig. S2.

Fig. 3a depicts the device structure of $CH_3NH_3PbI_3$-based solar cells, in which, $CH_3NH_3PbI_3$ was fabricated by hot-casting process on FTO glass substrates coated with block TiO$_2$ and m-TiO$_2$ layer. Subsequently, the Spiro-OMeTAD-based hole-transfer layer (80.0 mg spiroOMeTAD, 28.5 mL 4-tert-butylpyridine and 17.5 mL lithium-bis (tri-fluoromethanesulfonyl) imide (Li-TFSI) solution (520.0 mg Li-TFSI in 1.0 mL acetonitrile) all dissolved in 1.0 mL chlorobenzene) was deposited by spin-coating at 4000 rpm for 30 s. Finally, a 100-nm-