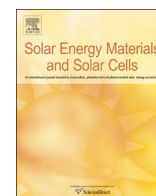




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Solvent-assisted growth of organic–inorganic hybrid perovskites with enhanced photovoltaic performances

Chongyang Sun^a, Yiping Guo^{a,*}, Huanan Duan^a, Yujie Chen^a, Yunlong Guo^b, Hua Li^a, Hezhou Liu^{a,*}^a State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China^b University of Michigan-Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, PR China

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ABSTRACT

Photoelectric conversion efficiency enhancement of the emerging highly efficient, low cost organic–inorganic perovskite solar cells, which is considered as a promising candidate in solar energy industry, has received great attention. And, it is investigated that the device performance can be significantly improved simply by a convenient morphology controlling approach aiming at obtaining uniform and high coverage of perovskite. However, reliable means to prepare high-quality perovskite layer remains to be a big challenge. In this work, we proposed a novel, simple and efficient method in optimizing the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films. Utilizing this excellent rapid fabrication process, our devices present an average power conversion efficiency of 9.65% with remarkable reproducibility, which is about 42% higher with respect to devices produced by regular protocol. This work sheds a light on enhancing performance of the state-of-the-art solar cells by exploring novel methods to prepare photoactive layers of high-quality.

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1. Introduction

Recently, organic–inorganic hybrid materials have been employed as a promising light harvester in solid thin film solar cells because of their suitable direct bandgap (~ 1.55 eV), large absorption coefficients ($\sim 10^5$ cm^{-1}) [1–9], outstanding charge transport characteristics of holes and electrons [8–10], large electron/hole diffusion lengths (over 100 nm) [8,9,11], and tunable electronic/optical properties by adjusting their inorganic or organic component [12–18]. In the past five years, the efficiency of lead halide perovskite solar cells has taken a huge leap forward from 3.8% to 20.1% [1,2,4,19–21] by the perfection of device architectures (e.g. mesoporous and planar cell configuration) or by different film deposition processes (e.g. one step spin-coating, sequential solution process [6], vapor-assisted solution processing [22] and vacuum deposition [23]). Compared with the regular one-step method and vacuum deposition, the sequential deposition method has more advantages of easy control and good repeatability. Therefore, it has become a popular method for preparing perovskite films. In the classical sequential deposition synthesis of perovskite (e.g. $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$), a flat and layered PbI_2 film is deposited onto the mesoporous or planar

substrate from a N,N-Dimethylformamide (DMF) solution, then dipped into an isopropanol (IPA) solution of $\text{CH}_3\text{NH}_3\text{I}$ (MAI) followed by annealing at an elevated temperature (e.g., 70 °C) to form $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃).

In the sequential deposition method, the crystal growth and film morphology of the final perovskite MAPbI₃ strongly depend on the surface morphology and crystallinity of initial PbI_2 film, and a big challenge is how to fully and rapidly convert PbI_2 to MAPbI₃. It is well known that the formation of high quality perovskite needs a compact PbI_2 precursor film, but it is difficult for MAI to inject into a compact PbI_2 film, rendering the unreacted and remnant PbI_2 on the final perovskite film [24–26]. In order to obtain a full conversion of PbI_2 to MAPbI₃, PbI_2 film must be soaked in MAI isopropanol solution for hours [27–29]. The long reaction time in MAI solution could lead to the dissolution (sometimes peeling off) of perovskite, decreasing the efficiency of the final devices. Several strategies have been developed to address this challenge, including using MAI vapor instead of MAI in IPA solution, controlling the crystallinity of the initial PbI_2 film, interdiffusion method to fabricate pin-hole free perovskite film, and thermal decomposition of thermally unstable stoichiometric $\text{PbI}_2\text{-CH}_3\text{NH}_3\text{Cl}$ ($\text{PbI}_2\text{-MACl}$) precursor film to form PbI_2 film [22,26,30–32]. These approaches improved the conversion rate of PbI_2 -to-MAPbI₃ and increased the reaction speed without causing

* Corresponding authors. Tel.: +86 021 34202593.

E-mail addresses: ypguo@sjtu.edu.cn (Y. Guo), hzhliu@sjtu.edu.cn (H. Liu).

significant degradation of the MAPbI₃ film during the conversion reaction process.

In this work, we develop a new solvent-assisted method to grow perovskite film on the basis of the typical sequential deposition for preparing high-quality perovskite films. In the regular two step approach, we find that the conversion speed of PbI₂-to-MAPbI₃ is slow without DMF addition. In contrast, by using the solvent-assisted deposition approach, in which the PbI₂ film was soaked in an IPA/DMF mixed solution of MAI at room temperature, the PbI₂ film can be rapidly converted to MAPbI₃ with high conversion rate which leads to improved device performance. It can be ascribed to the DMF-assisted effect, because DMF is a good solvent of PbI₂, a little amount of DMF can “activate” the flat and compact layered PbI₂ film without seriously destroying the structure and decreasing the properties of the final perovskite films.

2. Experimental details

2.1. Materials

Commercial TiO₂ nanoparticles (P25) were purchased from Degussa. Hydroiodic acid (57–58 wt% in water), methylamine (30–33 wt% in absolute ethanol), lead iodide (PbI₂) (99.9%), N,N-Dimethylformamide and isopropanol were purchased from Aladdin Reagents. 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-MeOTAD) (≥99.0%), Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI) (≥99.5%), and 4-tert-butylpyridine were purchased from Yingkou Optimal Choice Trade Co., Ltd. All of the used reagents were analytical grade, without further purification.

2.2. Synthesis of CH₃NH₃I and preparation of TiO₂ paste

CH₃NH₃I was synthesized according to the reported procedure [2,4,33], methylamine (25 ml, 30–33 wt% in absolute ethanol, Aladdin), hydroiodic acid (15 ml, 57–58 wt% in water, Aladdin) and 100 ml ethanol were mixed in ice bath for 2 h. After stirring at 0 °C for 2 h, the precipitation was recovered by a rotary evaporator. The crude product was washed with diethyl ether three times until no yellow residue remains, and finally dried at 60 °C in a vacuum oven for 24 h. TiO₂ paste was prepared by mixing the TiO₂ particles (P25) with terpineol (TP, 98%, Aladdin), ethyl cellulose (EC, 46cp, Sinopharm Chemical Reagent) and acetylacetone (ACAC, 99%, Sinopharm Chemical Reagent) at a nominal weight ratio of TiO₂:TP:EC:ACAC=1:3:0.5:0.1 in ethanol solution, and further treated with a ball mill for 48 h. After treated with ball mill, the ethanol was removed by a rotary evaporator at 50 °C.

2.3. Device fabrication

Fluorine-doped transparent conducting SnO₂-coated glass substrate (FTO, Wuhan Ge'ao, 14 Ω sq⁻¹) was patterned according to the previous procedure [34,35]. A compact hole-blocking layer [36] TiO₂ was deposited by spin-coating a mildly acidic solution of titanium isopropoxide in ethanol (2000 rpm, 40 s), and subsequently annealed at 500 °C for 30 min. The mesoporous TiO₂ substrate (304 ± 15.5 nm) was prepared by spin-coating a home-made TiO₂ paste (3000 rpm, 30 s), then annealed at 500 °C for 30 min, where the pristine paste was diluted in ethanol (0.45 g/ml). The mesoporous TiO₂ film was immersed in 40 mM aqueous TiCl₄ (>98%) solution at 70 °C for 30 min and annealed at 500 °C for 30 min again. CH₃NH₃PbI₃ was formed using two-step spin-coating procedure [6,37]. PbI₂ solution (1 M) was prepared by dissolving 462 mg PbI₂ (99.9%, Aladdin) in 1 ml anhydrous DMF (99.8%, Aladdin). Three 10 mg/ml MAI solutions were prepared in

blend solvent with 0%, 1%, 2% anhydrous DMF by volume of IPA and stirred for 2 h. PbI₂ solution (30 μl) was spin-coated on the mesoporous TiO₂ film at 6500 rpm for 10 s. After spinning, the film was dried at 70 °C for 3 min and then 100 °C for 5 min. The obtained films were dipped in CH₃NH₃I solution, then rinsed with 2-propanol and annealed at 100 °C for 10 min. A volume of 25 μl of spiro-MeOTAD solution [6] was spin-coated onto the MAPbI₃ perovskite layer at 4000 rpm for 30 s to fabricate the hole transporter layer (HTL). Finally, 140 nm of silver was thermally evaporated on the spiro-MeOTAD-coated film to complete the fabrication of the cell device. The active area of 0.11 cm² for the devices was determined by a shadow mask.

2.4. Device characterization

The morphology of the TiO₂ film and perovskite film was observed using a field emission scanning electron microscope (SEM, FEI-Sirion 200). The root-mean-square roughness of the perovskite films was measured by atomic force microscopy (AFM, NanoScope III microscope, Digital Instrument) in tapping mode. The thicknesses of the films were measured by a profilometer (Dektak 150, Veeco Instruments Inc.). The adhesion strength of perovskite films on the mesoporous TiO₂ substrate was measured by using the scotch test recommended by ASTM standard D3359-02 (method B) [38,39]. UV-vis spectra of the films were recorded by Agilent UV/vis spectrophotometer (model Cary 60). X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX 2400 diffractometer with Cu Kα radiation at scan rate of 5 degree/min under operation condition of 35 kV and 200 mA. Photocurrent and voltage were measured by a solar simulator (Oriel Sol 3A class AAA) equipped with a 450 W Xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. The NREL-calibrated Si solar cell with KG-2 filter was used to adjust light intensity into one sun illumination (100 mW/cm²). A black aperture mask [2,40,41] with the area of 0.09 cm² (3 × 3 mm²) to prevent scattered light was attached during photocurrent and voltage measurement. The electrochemical impedance spectroscopy (EIS) was carried out under 1 sun light illumination using Impedance/Gain-phase Analyzer (Solartron SI 1260) at a forward voltage bias of 0.7 V and with the frequency ranging from 100 kHz to 1 Hz. The magnitude of the alternative signal was 10 mV AC amplitude.

3. Results and discussion

High resolution scanning electron microscopy (HR-SEM) top view images of the mesoporous TiO₂ film and PbI₂ film are shown in Fig. S1. Note that the surface of the mesoporous TiO₂ film and the PbI₂ film is uniform and flat, which is suitable for preparing high quality perovskite films. The thicknesses of the mesoporous TiO₂ film and the PbI₂ film are measured by profilometer, and are determined to be 304 ± 15.5 nm and 80.8 ± 1.46 nm, respectively (as depicted in Fig. S2a and b). The deposition of MAPbI₃ on the mesoporous TiO₂ film is carried out by solvent-assisted two-step sequential deposition method, where the initial PbI₂ films were soaked into MAI solution in the mixed solvent of IPA/DMF. After annealing at 100 °C, the film becomes dark, indicating the formation of MAPbI₃. The ionic and covalent interactions between the metal cations and the halogen anions create inorganic octahedron, while the cationic alkylammonium head groups provide charge balance to the structure. UV-vis and XRD measurements were used to examine the time evolution of the conversion rate of PbI₂ into MAPbI₃. Fig. 1a shows the effect of different ratio of DMF in IPA on the XRD patterns with 1 min dipping in 10 mg/ml MAI. The PbI₂ residue all can be observed. This is evidenced by the existence of both PbI₂ and MAPbI₃, which matches well with the peaks

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