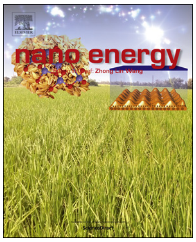
Nano Energy (2016) **19**, 17–26

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



COMMUNICATION

A halide exchange engineering for $CH_3NH_3PbI_{3-x}Br_x$ perovskite solar cells with high performance and stability

Weidong Zhu[a], Chunxiong Bao[a], Faming Li[a], Tao Yu[a,b,c,*], Hao Gao[a], Yong Yi[a], Jie Yang[a], Gao Fu[a], Xiaoxin Zhou[a], Zhigang Zou[a,b,c]

[a]*National Laboratory of Solid State Microstructures & Eco-Materials and Renewable Energy Research Center (ERERC) at Department of Physics, Nanjing University, Nanjing 210093, PR China*
[b]*Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, PR China*
[c]*Jiangsu Key Laboratory for Nano Technology, Nanjing 210093, PR China*

Received 20 July 2015; received in revised form 6 November 2015; accepted 19 November 2015
Available online 28 November 2015

KEYWORDS
$CH_3NH_3PbI_3$;
Halide exchange;
Post-treatment;
Perovskite solar cell;
Stability

Abstract
A facile halide exchange route based on CH_3NH_3Br solution post-treatment has been successfully employed to transform the two-step spin-coated $CH_3NH_3PbI_3$ films into the $CH_3NH_3PbI_{3-x}Br_x$ films, whose morphologies and compositions could be modified simultaneously. With the increase of CH_3NH_3Br solution concentration, the $CH_3NH_3PbI_{3-x}Br_x$ films exhibited increased grain size, prolonged charge carrier lifetime, and enlarged bandgap with slightly reduced light absorption compared with the parent $CH_3NH_3PbI_3$ film. The mesostructured perovskite solar cells based on the $CH_3NH_3PbI_{3-x}Br_x$ films yielded the optimal power conversion efficiency (PCE) of 14.25%, which is much higher than that of device with the parent $CH_3NH_3PbI_3$ film. In particular, the device based on the $CH_3NH_3PbI_{3-x}Br_x$ film retained up to 93% of its original PCE after exposed to air for 14 days without any encapsulation, presenting a favorable stability. Our work suggests a novel and attractive way to fabricate high-performance perovskite solar cells with excellent stability.

---

[*] Corresponding author at: National Laboratory of Solid State Microstructures & Eco-Materials and Renewable Energy Research Center (ERERC) at Department of Physics, Nanjing University, Nanjing 210093, PR China.
E-mail address: yutao@nju.edu.cn (T. Yu).

http://dx.doi.org/10.1016/j.nanoen.2015.11.024
2211-2855/

Introduction

Recently, perovskite solar cell as a new kind of photovoltaic (PV) devices has become a rapidly rising star due to the swiftly boosted power conversion efficiency (PCE), easy fabrication, and sufficient supply of raw materials [1-4]. Metal organic perovskite materials such as $CH_3NH_3PbI_3$ are the most important components in the cells. The investigations focused on these perovskite films have revealed their unique features, including high absorption coefficient [4,5], ambipolar charge transport properties [6,7], long carrier diffusion lengths [8,9], and low-temperature solution processability [10-12]. All such features are crucially important for their applications in high-performance and low-cost PV devices.

Critical to fabrication of perovskite solar cells, in particular mesostructured devices, is the realization of high-quality metal organic perovskite films [13-15], because the morphology and crystallinity of the films play an important role for the ultima device performances [16,17]. For example, Wang et al. [17] investigated the coverage of the $CH_3NH_3PbI_3$ capping layer on mesoporous TiO_2 layer and found the PCE of the devices increased with the increase of $CH_3NH_3PbI_3$ coverage. By controlling the cuboid size of $CH_3NH_3PbI_3$ capping layer, Park et al. [18] realized a device with the best PCE of 17.01%. Meng et al. [19] introduced a hot-pressing method to improve the morphology and crystallinity of $CH_3NH_3PbI_3$ capping layer, which resulted in significantly enhanced PV performances for both hole-transporting-material-free type and spiro-OMeTAD based solar cells. Besides improving the morphology and crystallinity of metal organic perovskites, chemical management of their compositional elements has been verified as an effective way to further refine their properties [3,20-23]. Specifically, mixture of multiple halogen elements in metal organic perovskites can bring at least three positive effects [24]. The first is boosting their stability. In the seminal work of Lee et al. [6], they found that $CH_3NH_3PbI_{3-x}Cl_x$ was remarkably stable compared with $CH_3NH_3PbI_3$ when processing in air. Noh et al. [20,25] also revealed that incorporating Br into $CH_3NH_3PbI_3$ could effectively improve the devices' stability. The second is improving the carrier transport properties of metal organic perovskite films, thus the device performances. It has been revealed that $CH_3NH_3PbI_{3-x}Cl_x$ possessed much longer carrier diffusion length than $CH_3NH_3PbI_3$ [8,26]. Besides, the $CH_3NH_3PbI_{3-x}Br_x$ and $CH_3NH_3PbBr_{3-x}Cl_x$ were confirmed having improved carrier mobility and reduced carrier recombination rates [27-29]. The third is increasing the open circuit voltage (V_{oc}) of the devices. Previous works reported that the V_{oc} for solar cell with $CH_3NH_3PbBr_3$ ($CH_3NH_3PbBr_{3-x}Cl_x$) can reach as high as 1.3 V (1.5 V) [28,30,31]. Apparently, by modifying the morphology and/or composition of metal organic perovskite films, the performance of perovskite solar cells can be effectively improved.

Since the discovery of the ion exchange reaction of inorganic nanocrystals by the Alivisatos [32], much attention has been paid to the simultaneous modulation of composition and micro-structure of inorganic nanocrystals as well as nanostructured films via this type reaction [33-37]. More recently, Pellet et al. found that when the metal organic perovskite with the formula $CH_3NH_3PbX_3$ (X=Cl, Br, or I) was infiltrated in a mesoscopic scaffold, halide exchange on the perovskite lattice was strikingly fast, being completed within seconds or minutes after contact with the halide solution [38]. Similarly, Solis-Ibarra et al. [39] revealed that post-synthetic halide conversion can occur in both three- and two-dimensional metal organic perovskites. Inspired by these interesting results, we expect that it is possible to simultaneously modify the morphology and compositional elements by post-synthetic halide exchange, thus improving the PV performance of perovskite solar cell.

In this study, a facile halide exchange route has been successfully employed to prepare $CH_3NH_3PbI_{3-x}Br_x$ films from the two-step spin-coated $CH_3NH_3PbI_3$ films reacted with CH_3NH_3Br solution, which allows modifying the films' morphologies and compositions simultaneously. Compared with the parent $CH_3NH_3PbI_3$ film, the $CH_3NH_3PbI_{3-x}Br_x$ films exhibited increased grain size, prolonged charge carrier lifetime, and enlarged bandgap with slightly reduced light absorption with the increase of CH_3NH_3Br solution concentration. The PCE of the mesostructured perovskite solar cells based on the $CH_3NH_3PbI_{3-x}Br_x$ films could be optimized to be 14.25%, which is much higher than that of device with the parent $CH_3NH_3PbI_3$ film. In particular, the PCE of device based on the $CH_3NH_3PbI_{3-x}Br_x$ film could retain up to 93% after exposed to air for 14 days without any encapsulation.

Experimental section

Materials

Lead iodide (PbI_2, 99.999%), Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI, 98%) and 4-tert-butylpyridine (TBP, 98%), dimethylformamide (DMF, anhydrous 99.5%) were purchased from Aladdin Reagents. Isopropanol (IPA), diethanolamine, chlorobenzene, acetonitrile, tetrabutyl titanate and were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 2, 2′, 7, 7′-tetrakis (N,N-di-p-methoxy-phenylamine)-9,9′-spirobifluorene (spiro-MeOTAD, $\geq$99%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. (China). Hydroiodic acid (47 wt% in water), hydrobromic acid (48 wt% in water) and methylamine (33 wt% in absolute ethanol) were purchased from Sigma-Aldrich. CH_3NH_3Br and CH_3NH_3I were synthesized by the recipe reported previously.

Solar cell fabrication

Preparation of the mesoporous TiO_2 films: Fluorine-doped tin oxide (FTO) glass substrates with sheet resistance of about 14 Ωsq^{-1} were cleaned by ultrasonic washing in detergent solution, acetone, absolute alcohol, and deionized water for 30 min in succession, and then cleaned by UV-ozone treatment for 30 min. 30 µL TiO_2 sol was spin-coated on the pre-cleaned substrates to form compact TiO_2 layers with the thickness of about 60 nm by annealing at 480 °C for 40 min in air. 30 µL diluted TiO_2 paste was then dropped onto the TiO_2 compact film to form mesoporous TiO_2 layer with the thickness of about 200 nm by spin-coating at 5000 rpm for 30 s, followed by annealing at 500 °C for 30 min in air.