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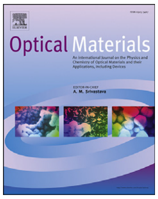

Effect on the morphology and optical properties of $CH_3NH_3PbI_3$ with additive of NH_4Cl

Xiaoliang Yan, Xiao Yang, Ruizhi Wang, Heng Li**, Chuanxiang Sheng*

School of Electronic and Optical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, PR China

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Rapid emergence of solar cells based on mixed organic-inorganic halide perovskite have led to high power conversion efficiencies of over 20% in recent years. Looking for a simple and convenient way to fine-control of the perovskite film morphology is becoming one of the main issues. In this work, we explore the effect of adding NH_4Cl on crystallization process and optical properties of perovskite. With adding NH_4Cl, the perovskite films prepared by one-step method present better morphology than films without adding NH_4Cl, namely, smoother surface and better coverage which result in uniform and much more stable photoluminescence intensities as well as longer lifetime of photoexcitations. More importantly, the photovoltaic cells fabricated with the addition of the NH_4Cl have far better performance than the cells without additives. Therefore, one-step fabrication method can also control the morphology of perovskite films finely for both optical application and solar cells with adding proper additive.

1. Introduction

Recently, organic-inorganic hybrid perovskite solar cells with outstanding photoelectric conversion performance which increases from 3.8% to more than 20% [1–11] within six years have attracted considerable research attentions. The current record efficiency is 22.1% [12], which is close to the values from solar cell of single crystal silicon and of CuInGaSe thin film [13]. However, the true advantage of perovskite solar cell may be the simple and cheap process of fabrication. One-step precursor solution deposition is the simplest way to fabricate perovskite film as active materials, compared to other fabrication methods such as two-step sequential solution deposition, dual-source vapor deposition [14,15]. On the other hand, one-step method often generates the tree-like morphology with many pinholes [16,17], increasing the leakage current then decreasing and even destroying the performance of corresponding devices [18,19]. Recently, it was reported that adding NH_4Cl to the precursor solution improve the power conversion efficiencies of perovskite solar cells prominently [20], even with much less annealing time than many other existing methods [24]. Nevertheless much less attention has been paid to study the optical properties of perovskite film after adding NH_4Cl in the process of deposition, which however would be crucial in understanding and furtherly enhancing the performance of solar cell using one-step methods.

In this work, we prepared perovskite thin film with one-step precursor solution deposition and certified that adding NH_4Cl has remarkable effect on the morphology and optical properties in perovskite films, resulting in the probably best cost-effective method for fabrication of perovskite solar cells.

2. Experimental

2.1. Preparation of perovskite precursor

Perovskite precursor solution was prepared by dissolving PbI_2 and CH_3NH_3I (MAI) in N,N-dimethylformamide (DMF) with equimolar ratio. The additional NH_4Cl was added to the mixture solution with the molar ratio of 1:1:0.5. The mixed solution in DMF (35%) was stirred overnight at 60 °C inside a nitrogen-filled glove box with oxygen and moisture levels < 1 ppm.

2.2. Device fabrication

The ITO substrate (15 Ω square^{-1}) were pre-cleaned in an ultrasonic bath with deionized water, acetone and isopropanol in sequence for 15 min respectively, then a nitrogen flow was used to

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* Corresponding author.
** Corresponding author.
E-mail addresses: hengli@njust.edu.cn (H. Li), cxsheng@njust.edu.cn (C. Sheng).

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dry the ITO substrate. Finally the ITO substrate was treated with UV-ozone for 30min. PEDOT:PSS film was deposited by spin-coating at 3000 rpm for 60s on the ITO substrate and then dried at 120 °C for 15min in the air, and then the substrates were transferred into a N_2 glove box. $CH_3NH_3PbI_3$ precursor solution without additive and with NH_4Cl was spin-cast at 3000 rpm for 60s and heated at 100 °C for 30s, respectively. $PC_{61}BM$ solution (20 mg/mL in chlorobenzene) was then spin-coated onto $CH_3NH_3PbI_3$ layer at 2000 rpm for 30s. Finally silver (100 nm) was deposited on $PC_{61}BM$ layer through a shadow mask under vacuum (ca. 10^{-4} Pa). The effective area for the perovskite solar cells is 6 mm^2. All perovskite films for the following discussion were prepared via one-step solution method under the same conditions except adding additives or not in perovskite precursor solution. Unless otherwise stated, all materials were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate(PEDOT:PSS) was purchased from Clevious.

2.3. Characterization

XRD patterns of perovskite films were obtained by using a Bruker AXS Dimension D8 X-ray System. A scanning electron microscope (SEM, FEI Quanta 250FEG) was used for recording the SEM images. The absorption spectra of perovskite film were measured by EVOLUTION220 UV–vis spectrophotometer. For photoluminescence (PL) and photoinduced absorption (PIA) spectra obtained using a standard cw setup [21–22], the film was in the dynamics vacuum of about ~0.2 Pa. A continuous wave (CW) diode laser at $\lambda = 447$ nm was used as excitation source, and an incandescent tungsten/halogen lamp as the probe. The pump and probe beams were overlapped on the sample in a cryostate, the transmitted probe beam was filtered through a monochromator and detected by a Si photodiodes. I–V measurements were carried out with a Keithley 2400 source meter under the simulated AM 1.5G illumination (100 mW/cm^2; Solarbeam-02-3A Class AAA Solar Simulator). A solar cell IPCE text system (CROWNTECH,INC. QTEST STATION 500AD) was used to determine the incident-photon-to-current efficiency.

In optical measurements, The excitation source was either a pulsed Nd:YAG laser with pulse duration of 7 ns at 532 nm for time resolved measurements or a CW diode laser with wavelength at 447 nm for quasi-steady-state measurements. For time-resolved PL dynamics, the emission was collected by a 1 GHz Si amplified photodetector; for transient photoinduced absorption dynamics, the probe bean was a continuous-wave diode laser at 760 nm, which was collected by a fast photodetector for PL emission. Finally both PL and ΔT signals were recorded by a digital oscilloscope with the bandwidth of 1 GHz, which was synchronized with a trigger from a fast photodetector irradiated by a small fraction of pulsed laser. The time resolution was about 20ns for both transient PL and PIA dynamics. For quasi-steady-state photoinduced absorption (PIA) measurement, the probe beam was provided by incandescent tungsten/halogen lamp. The change of the transmitted probe beam, which was caused by the modulated pump beam, was filtered through a monochromator and detected by a Si photodiodes and a lock in amplifier. For micro-PL measurements, the excitation light from a continuous wave (CW) solid state laser at $\lambda = 532$ nm was focused on a film using 50 microscope objective with N.A. of 0.55, which was also used to collect the PL. The excitation power was 2.2μw and laser spot size was about 2 μm. The film was put on 1-axis motorized translation stage with minimum step of 3 μm.

3. Results and discussion

3.1. XRD and SEM results

Fig. 1(a) shows that the film with adding NH_4Cl shows smoother surface and more pervious to light than the film without adding NH_4Cl (as No additive in figure). XRD measurements were used to verify the crystallization of perovskite films. Fig. 1(b) presents the XRD patterns of the perovskite films with and without adding NH_4Cl, the XRD peak position for the different perovskite films are nearly the same, The appearance of strong diffraction peaks located at $2\theta = 14.2°$and 28.5° was observed corresponding to the planes of (110) and (220) [23]. However, the XRD peak intensity of the perovskite film prepared with the NH_4Cl additive is about three times stronger than that of the film without any additive, suggesting that the NH_4Cl additives favored $CH_3NH_3PbI_3$ crystallization. Previous measurements are further supported by scanning electron microscopy (SEM) images. $CH_3NH_3PbI_3$ films prepared using no additive is discontinuous with low surface coverage, needle-like crystals and large voids can be clearly seen in Fig. 1(c). By adding NH_4Cl, the film became uniform and presents much better coverage (Fig. 1(d)).

3.2. Photovoltaic devices

The planar perovskite solar cells with a structure of ITO/PEDOT:PSS/Perovskite/$PC_{61}BM$/Ag were fabricated to probe the effect of additives on photovoltaic performance. The device fabricated without additive added in perovskite film exhibited an open-circuit voltage (V_{oc}) of 455 mV, a short-circuit current density (J_{sc}) of 2.6 mA/cm^2, a fill factor (FF) of 39% and a power conversion efficiency (PCE) of o.57%. On the other hand, the device using NH_4Cl additive gave a V_{oc} of 900 mV, a J_{sc} of 16.2 mA/cm^2, a FF of 56% and PCE of 7.83%. The measured device performance data are summarized in Table 1. This consequence was due to the perovskite adding NH_4Cl would result in a higher crystalline, more uniform and smoother perovskite film in contrast to the film without additive, as we have presented in Fig. 1. Fig. 2(a) displayed the current density versus voltage (J-V) curves of photovoltaic cells fabricated both with and without the addition of the NH_4Cl, respectively. Fig. 2(b) showed the corresponding incident-photon-to-current efficiency (IPCE) spectrum for the device fabricated with additive and without (multiplied eight for comparison), respectively. All these characteristic parameters could verify that perovskite solar cells adding NH_4Cl show much better performance than those without additive.

3.3. Absorption and photoinduced absorption spectroscopy

In order to illuminate the mechanism for the better photoelectric properties of the perovskite film adding NH_4Cl, we conducted the measurements of optical properties on corresponding active materials. The UV–vis absorption spectra of the perovskite film with and without additive are showed in Fig. 3(a), the film prepared using no additive showed slight red shift, which might be due to the poor crystallization of $CH_3NH_3PbI_3$ in the film [25]. Using Tauc analysis [26–27] showed in Fig. 3(b), we could estimate $E_g = 1.57$ eV of the perovskite film without additive and $E_g = 1.59$ eV of the film adding NH_4Cl. Further information will be achieved through the Urbach analysis [28–29] according to the description of absorption edge exponent with expression of $E_u = h\nu/\ln(\alpha)$. Then Urbach energy, E_u of the perovskite film with and without additive equals 84 meV and 92 meV, respectively (Fig. 3(c)). The smaller Urbach energy in $CH_3NH_3PbI_3$ films prepared using NH_4Cl suggests a lower degree of structural disorder and less defects compared to $CH_3NH_3PbI_3$ films prepared without additive [30–31]. In addition,