High performance CH$_3$NH$_3$PbI$_3$-based photodetector fabricated in ambient condition by doctor-blading deposition

Shuigen Li$^1$,*, Guangxiong Qiu$^1$, Xiangyu Xie$^1$, Cheng Li$^1$, Haiyan Fu$^1$, Runsheng Wu$^1$, bingchu Yang$^{2,**}$

$^1$School of New Energy Science and Engineering, Xinyu University, Jiangxi, Xinyu 338004
$^2$School of Physics and Electronics, Central South University, Hunan, Changsha 410083

*Corresponding author’s e-mail: lishuigen@xyc.edu.cn
**Corresponding author’s e-mail: bingchuyang@csu.edu.cn

Abstract. High-quality CH$_3$NH$_3$PbI$_3$ perovskite thin films in air via doctor-blading technology of in-situ heat treatment were prepared, the resulting perovskite film has the advantages of large crystal domains, good stability and repeatability. Based on the perovskite film, the perovskite photodetectors with such a simple structure of glass/CH$_3$NH$_3$PbI$_3$/Au were constructed, and the high resulting responsivity (R) of 5.70 AW$^{-1}$ was achieved, the as fast as rise and fall response speed of 14.0ms and 13.4ms were showed, which indicates that the perovskite films via doctor-blading have a potential application prospect in constructing low-cost and large-area optoelectronic devices.

1. Introduction

As an important photoelectric device, Photodetector is widely used in optical communication, environmental monitoring and so on [1-2]. Recently, organic-inorganic hybrid perovskite has attracted extensive research interest for its suitable direct band gap, high absorption coefficient, long electron hole diffusion length and carrier life, as well as excellent charge transfer characteristics. The perovskite material was discovered about 36 years ago[3] and was first used to make the active layer material for solar cells in 2009, achieving a power conversion efficiency of 3.8% for solar cells[4]. Due to the excellent light absorption characteristics of perovskite materials, photodetectors based on perovskite materials have been developed rapidly. So far, the conversion efficiency of perovskite solar cells has been taken a great breakthrough [5-7]. At the same time, various techniques for preparing high quality perovskite films have also been developed. Among them, spin coating process is a common process combining with solution technology and gas phase treatment to obtain high-quality perovskite film[8]. This process has also been introduced into the preparation of photovoltaic detector and thus produce fine photovoltaic detection performance[9-10]. In addition, the vapor deposition technology is also a technology to prepare high performance perovskite thin films[11]. Spin coating or vapor deposition processes are generally used to construct small areas of perovskite films, which are incompatible with building large-areas perovskite films and finally realizing industrial production. On the other hand, roll-to-roll printing, ultrasonic spraying and inkjet printing have advantages in the production of large-area perovskite films. However, the quality of the films is not as good as the traditional preparation technology.
The doctor-blading process has been applied to the formation of perovskite films in photoelectric device due to its advantages of simple process and low cost. In particular, this process can be matched with a roll-to-roll technique based on a flexible substrate [12-13]. Nowadays, the preparation of high performance perovskite solar cells via doctor-blading has achieved good results [14] and has been applied to the preparation [15] of large area perovskite solar cells. However, to avoid the influence in the air, the doctor-blading process is generally carried out in the glove box. In order to accelerate the popularization and application of high-performance organic-inorganic perovskite materials, this study adopts the coating process under air environment to make perovskite thin film material, and thus the photodetector was constructed based on the perovskite active layer, then the performance and influencing factors of the device are deeply studied.

2. Experiment

The appropriate amount of CH₃NH₃I and PbI₂ was mixed in a 1:1 molar ratio and dissolved in N,N-dimethyl formyl ammonium (DMF) to obtain the precursor solution. A precursor solution was stirred at 70°C for 12h to obtain a homogeneous and transparent solution, filtered it.

In the first place, the glass substrate was washed with deionized water for 15 minutes. Then ultrasonic wash with acetone for 15 minutes and rinse with deionized water for 10 times. Next with isopropanol for 15 minutes, and finally dried naturally. The cleaned glass substrate was exposed to ultraviolet radiation and treated for 20 minutes.

The temperature of the scraper is adjusted to 120°C before doctor-blading, and the distance between the glass substrate and the blade of a scraper is set to 100 μm. The glass substrate is preheated on the scraper for 2-3 minutes under 120°C. During doctor-blading, 15 μL of precursor droplets is dripped on the preheated glass substrate. When scraped, the black perovskite film is formed, then remove the formed perovskite film and retained directly without subsequent annealing. In this process, perovskite films with large crystalline domains form rapidly with the volatilization of solvents. Lastly, 90 nm of gold electrode was evaporated onto the perovskite film covered with a mask plate, forming 80 μm wide, 1000 μm long photodetector with effective active area of 0.008 cm².

All the samples were tested in air, and the morphology of the samples was detected by optical microscope and scanning electron microscope. XRD was used to detect the crystal structure of perovskite film, and the scanning rate was 0.02°/min. UV VIS spectrometer was used to measure the optical absorption property of the film. The steady-state luminescence spectrum (PL) was excited by a 400 nm laser, and the laser was generated by a femtosecond pumped laser. The performance of the photodetector is tested using a probe table connected with a semiconductor parameter analyzer.

3. Results and discussion

To construct high-performance photodetectors, high-quality perovskite films are essential. During doctor-blading process, the quality of CH₃NH₃PbI₃ perovskite film can be controlled by solution concentration, scraper running speed, distance between scraper and substrate, and temperature of in situ heat treatment. Figure 1 show the formation of CH₃NH₃PbI₃ film by doctor-blading deposition. During the process, the concentration of the precursor solution is 550 mg/ml, and the linear contact is formed when the scraper is in contact with the solution, In which the distance between the scraper and the substrate is about 90 μm. Based on in situ heating, the solvent was rapidly volatilize and CH₃NH₃PbI₃ film can be formed within a short time.
Figure. 1 (a) Schematic of precursor solution dripping at one end of glass substrate, (b) scraping to prepare dense pin-free film, (c) structure of photodetector based on CH$_3$NH$_3$PbI$_3$ film.

To study the effect of in situ heat treatment temperature on film formation in doctor-blading process, the film formation at 100°C-120°C was investigated. Figure 2(a), 2(b) and 2(c) shows the morphology of CH$_3$NH$_3$PbI$_3$ films formed at different temperatures. It is showed that the area of crystal domain of the film formed is smaller at 100°C, the crystal domain increased with the rising temperature. To prevent decompose at high temperature, the temperature was controlled at 120°C. The XRD pattern of CH$_3$NH$_3$PbI$_3$ fabricated at 120°C is shown in Figure 2d, series diffraction peaks are exhibited at 14.3°, 18.9°, 22.7°, 24.7° and 32.2°, which could be attributed to the reflections of (110), (112), (211), (202) and (310) lattice plane for CH$_3$NH$_3$PbI$_3$ film.[8] The sharp diffraction peaks rooted the formation of well-crystallized CH$_3$NH$_3$PbI$_3$ perovskite film obtained by doctor-blading process.

Figure. 2 Film morphology under different temperatures (a) 100°C, (b) 110°C, (c) 120°C and (d) XRD of films formed at 120°C.

The SEM morphology of CH$_3$NH$_3$PbI$_3$ perovskite films are exhibited in Figure 3(a). The large domain area is composed of many grains with flat surface and good coverage (Figure 3(b)). It shows that the process can obtain large grain size leading to the formation of low film defects[16]. The UV-VIS absorption of CH$_3$NH$_3$PbI$_3$ perovskite via doctor-blading deposition is shown in Figure 3(c). It discovered that the CH$_3$NH$_3$PbI$_3$ film has good optical absorption performance from the visible region to the near-infrared region. At wavelengths less than 520 nm region, the optical absorption intensity of perovskite film is obviously enhanced. The perovskite film shows some advantages until about 780 nm.
The time-resolved PL of CH$_3$NH$_3$PbI$_3$ film shown in Figure 3(d) is about 9 ns. Studies have shown that the crystal quality in the perovskite film has a great influence on the carrier separation and transport. The large grain size means that the photogenerated carriers have a smaller carrier recombination rate [17].

![Figure 3](image)

Figure 3  (a)(b) perovskite films SEM morphology, (c)UV-VIS absorption spectra, (d) PL time decay trace with the exponential fits.

The photodetectors based on CH$_3$NH$_3$PbI$_3$ film via doctor-blading deposition were fabricated figure 1(c), In which a simple sandwich structure was constructed and CH$_3$NH$_3$PbI$_3$ active layer formed an ohmic contact with electrodes. As shown in figure 4, the photodetector shows a dark current approximately 0.006μA at 10V, but the photocurrent were rapidly increasing under the light-struck of 365nm, 532nm and 808nm. At the wavelengths of 532nm, the device produces a photocurrent of about 7μA, 1000 times the dark current (three orders of magnitude).

The performance of photodetector can be evaluated by characteristic data, in which optical response $R$ is an important performance parameter in photodetector. Here, $R=(I_{\text{light}}-I_{\text{dark}})/PS$, where $I_{\text{light}}$ represents the light current, $I_{\text{dark}}$ is the dark current, $P$ and $S$ are the incident light intensity and the effective illuminated area, respectively. Compared to UV and VIR regions, the photodetector exhibits much larger $R$, and the peak value is about 7A at 532nm. However, the photodetector has a large $R$ value at the low intensity, which indicates that the photodetectors of the CH$_3$NH$_3$PbI$_3$ material are more sensitive to the weak light. In addition, the device shows excellent light response to visible light, but it is insensitive to ultraviolet light and near infrared region light. Under 532 nm, the response of the photodetector can reach 5.70 A/W, which is much less at 365 nm and 808 nm.
Figure 4. (a), (c), (e) I-V characteristics of CH3NH3PbI3 perovskite photodetectors, (b), (d), (f), Photocurrent vs light power intensity at different wavelength.

Repeatability and response speed, the other two factors for photodetectors, can determine the alerting ability. The time dependent response for CH3NH3PbI3-based photodetectors was studied, which displayed a stable reversible conversion performance with 532 nm illumination on and off, (Figure 5(a)). The photoresponse of a single typical normalized cycle is shown in Figure 5(b), in which the fast response within a rise time (t1 = 14.0 ms) and fall time (t2 = 13.4 ms) was achieved. Here, the rise and fall time refers to the time when the photogenerated current changes between the minimum and 90% of the maximum.
Figure 5  (a) The time-dependent photocurrent measurement for CH$_3$NH$_3$PbI$_3$-based photodetector at 532 nm illumination, (b) the photocurrent response excited from 532nm, the rise and decay time is 14.0ms and 13.4ms.

4. Conclusions
Via low-cost doctor-blading deposition by in-situ heat treatment and without any additives, high-quality pin-hole free CH$_3$NH$_3$PbI$_3$ film with good coverage generated very quickly. In ambient condition, the high-performance CH$_3$NH$_3$PbI$_3$ photodetectors were fabricated, showing responsivity as high as 5.70A/W, and impressive response time of 14 ms, which indicates that perovskite materials are provided with good application potential in preparing low-cost, efficient and large-scale optoelectronic devices. This research disclosed that doctor-blading deposition process provides a significant technique for fabricating high-performance CH$_3$NH$_3$PbI$_3$ film, and its applications for optoelectronic devices.

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