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BCP influenced crystallization of $MAPbI_{3-x}Cl_x$ for enhanced power conversion efficiency and stability in perovskite solar cell

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ABSTRACT

A novel BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenan throline) - $MAPbI_{3-x}Cl_x$ composite light absorption film was fabricated to enhance the performance of perovskite solar cell (PSC). Compared with the device without BCP in $MAPbI_{3-x}Cl_x$ layer, the charge separation and transport and the quality of $MAPbI_{3-x}Cl_x$ film improved with the addition of BCP. The power conversion efficiency (PCE) increased from 10.69% to 16.25% with an optimized ratio of BCP additive. A reduced *J-V* hysteresis was simultaneously exhibited by the perovskite solar cell with a planer structure of FTO/TiO_2/perovskite film/Spiro-OMETAD/Ag. These enhanced performances are owing to smoother surface coverage, smaller series resistance and stronger charge separation, as BCP is used as additive. This work provides a new method to modify and improve the performance of planer perovskite solar cells.

1. Introduction

Owing to high-performance and cost-effectiveness, organic-inorganic perovskite solar cells are a promising class of new generation of solar cells capable of addressing the issue of energy resource scarcity the world faces today [1–5]. Within a short period of research and development, the PCE of perovskite solar cell has exceeded 20% [3–6]. This feat has been traced to the numerous fascinating properties of the perovskite layer which include; decent electron and hole mobility, wide range visible light absorption and long exciton diffusion length [1,7,8]. However, issues such as poor film crystal quality and poor coverage are common with $MAPbI_3$ perovskite film [9–13]. $MAPbI_{3-x}Cl_x$ perovskite film is unique as film compactness is ensured with the presence of an exited chloride ion [9]. Therefore, the $MAPbI_{3-x}Cl_x$ perovskite material is more widely used as light absorption film. As known, film quality and charge separation are crucial to the performance of planer perovskite solar cell. As a result, the issue of film quality and charge separation is being given much attention by various research groups. There also exist many reports on the optimization of film quality and charge separation. Such efforts include: interface engineering [15,17,18,23,40], annealing [2,11,14,16], use of additives [12,19,20] and so on.

Using additives, there exist two main fabrication methods for the optimization of film quality and charge separation. One is by assisted crystallization pathway. This involves the addition of intermediate phases such as BmPyPhB [20], HBr [12] and HI [21] which are subsequently removed in the final light absorption film. The addition gives an effectual assistant [12,20]. The other method is by placing the additive such as: salt, polyethylene glycol and $A_{10}C_{60}$ into the perovskite precursor solution and retaining it in the final light absorption film [22,24,49]. The two methods are both in order to improve film quality and charge separation.

In this work, we adopted BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenan throline) as additive and fabricated a BCP-$MAPbI_{3-x}Cl_x$ composite film. The composite structure is a dispersion of BCP in $MAPbI_{3-x}Cl_x$ perovskite films. Due to film quality and charge separation, we proposed that dispersing the BCP into $MAPbI_{3-x}Cl_x$ perovskite films could enhance the quality of $MAPbI_{3-x}Cl_x$ perovskite films and improve its charge separation and transmission. Consequently, a BCP-$MAPbI_{3-x}Cl_x$ light harvester film with better coverage and compactness was fabricated. As a result, the PCE of the perovskite solar cell increased from 10.69% to 16.25%. The series resistance (R_s), parallel resistance (R_{sh}) and hysteresis were also significantly reduced.

2. Experimental section

2.1. Solar cell fabrication

TiO_2-sol was synthesized following a previous report [25].

BCP-$MAPbI_{3-x}Cl_x$ perovskite precursor solution synthesis: Varied amounts of BCP (0–1200 μg/mL) (Sigma-Aldrich, 99.9%) were dissolved in 1 mL of DMF (N, *N*-dimethylformamide) at 80 °C for 5 h on a hotplate, MAI and $PbCl_2$ (Sigma-Aldrich) were added into each BCP

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solution at a 3:1 mol ratio and 30 wt%. The precursor solutions were heated at 60 °C for 12 h on a hotplate.

70 mg/mL solution of Spiro-OMETAD (Xi'an Polymer Light Technology Corp.) hole transport material was prepared in chlorobenzene. 17.6 μL 4-*tert*-butylpyridine (4-TBP) and 12.5 μL bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) (520 mg/mL of acetonitrile solution) were then added into the Spiro-OMETAD solution [17].

The structure of the fabricated solar cell is FTO/TiO_2/BCP (x)-$MAPbI_{3-x}Cl_x$/Spiro-OMETAD/Ag where "x" is the density of BCP solution. The device fabrication steps are as follow:

FTO-coated glass substrates were successively cleaned with distilled water, EtOH and acetone in an ultrasonic bath. The surfaces of the cleaned FTO-coated glass substrates were treated with oxygen plasma at 50 W for 5 min. A conductive TiO_2 (0.2 mol/L) was deposited on the treated FTO-coated glass substrates at 3000 rpm for 20 s by spin-coating. The films were placed in a muffle furnace at 400 °C for 30 min for complete crystallization. The furnace was allowed to cool to room temperature. The substrates were removed and transferred into a glove box filled with nitrogen. The BCP-$MAPbI_{3-x}Cl_x$ precursor solutions were spin-coated on the TiO_2 films at 3500 rpm for 30 s. The films were left for 20 min without heating. Whereafter, the films were annealed at 100 °C for 60 min on a hotplate to ensure the crystallization of $MAPbI_{3-x}Cl_x$. The Spiro-OMETAD based hole transport material was deposited at 3000 rpm for 30 s. The films were then put into a drying vessel overnight for the oxidization of Spiro-OMETAD. Finally, silver cathode was thermally evaporated on the Spiro-OMETAD layer at 1 Å/s. The thickness of the silver cathode was 100 nm. A device active area of 0.1 cm^2 was created with a shadow mask during evaporation. Reference devices were also fabricated with the same method.

2.2. Measurements and characterization

Current density-voltage (*J-V*) and Current density-time data were measured with an AM1.5G solar simulator (100 mW cm^{-2}, Sciencetech Inc., SS-150) and a Keithley 2400 source meter, under illumination. The light intensity of solar simulator was calibrated by standard Si solar cell. The external quantum efficiency (EQE) spectra of devices were measured by a certified IPCE instrument (Beijing 7-Star Optical Instruments Co., Ltd.) without bias light. The impedance spectroscopy was measured by a FRA equipped PGSTAT-30 from Autolab. Surface morphologies of $MAPbI_{3-x}Cl_x$ films were characterized with a scanning electron microscope (FEI Quanta 250). The Uv–vis absorption curve was recorded on a Uv–visible spectrophotometer (Jasco V-570). X-ray diffraction (XRD) patterns were achieved using a D/max-2400 X-ray diffraction spectrometer (Rigaku, Japan). All measurements were taken in air. All measurements of light intensity were under AM1.5G solar simulator (100 mW cm^{-2}, Sciencetech Inc., SS-150).

3. Results and discussion

Improvement in film quality is known to generate more photo-induced charge and an improvement in photoinduced charge separation enhances the performance of a planer perovskite solar cell. The addition of an organic material can enhance the quality of film [39] and the creation of decent heterojuntion can enhance charge separation and transmission [31]. To form an effective heterojuntion with $MAPbI_{3-x}Cl_x$, materials need to possess wider bandgap, more appropriate band edge and non-volatile character. Furthermore, owing to the good hole transfer capability of $MAPbI_{3-x}Cl_x$ [8], the additive should also be able to function as a hole blocking agent. BCP was selected as additive since it possesses lower valence level, higher conduction band level and wider bandgap than $MAPbI_{3-x}Cl_x$, PCBM and spiro-OMeTAD [42–44]. Based on these, a BCP-$MAPbI_{3-x}Cl_x$ composite perovskite solar cell is fabricated. Fig. 1 presents the fabricated multilayer PSC device structure. Owing to lower valence level of BCP [26] compared to $MAPbI_{3-x}Cl_x$ [18], a high potential barrier of BCP-$MAPbI_{3-x}Cl_x$ is formed in the light harvester film. Hole is blocked with the conduction band edge of BCP. Meanwhile the amount of electron transported from $MAPbI_xCl_{3-x}$ into BCP is optimized. There exists some reports on such functions of BCP [26–28]. Thus, the BCP shows electron transport and hole blocking capabilities [27–30]. It is favourable to the charge separation and transmission, it also ensures a balance of electron and hole flux in perovskite solar cell.

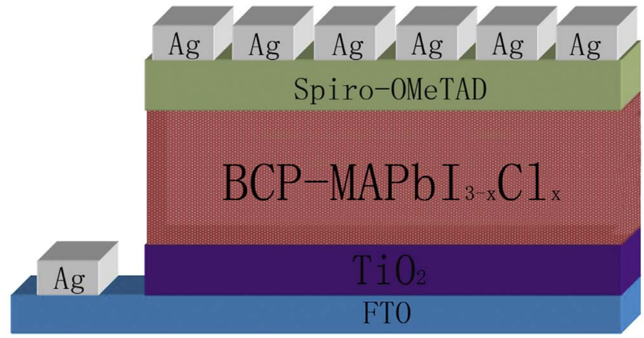

Fig. 1. Schematic diagram of the fabricated multilayer PSC.

Fig. 2 (a) shows the Uv–vis absorption curves of $MAPbI_{3-x}Cl_x$ and $MAPbI_{3-x}Cl_x$:BCP films. They agree well with previous reports on the absorption characteristics of $MAPbI_{3-x}Cl_x$ [11,12,31]. The edge of absorption curves is around 800 nm. There is no obvious absorptive peak in Uv–vis absorption curve and Raman spectra of $MAPbI_{3-x}Cl_x$:BCP (Fig. 2 (a) and (b)). The similarity observed in the absorptive peaks on the Raman spectra illustrates that there exists no unexpected byproduct or a chemical reaction between $MAPbI_{3-x}Cl_x$ and BCP [32]. Fig. 2 (c) shows X-ray diffraction patterns of $MAPbI_{3-x}Cl_x$ and $MAPbI_{3-x}Cl_x$:BCP. The patterns show the characteristic peak of the $MAPbI_{3-x}Cl_x$ at 14.17° and 28.51° [15]. The absence of PbI_2 peak at 12.23° confirms the complete crystallization of $MAPbI_{3-x}Cl_x$. Stronger diffraction peaks are observed for $MAPbI_{3-x}Cl_x$:BCP at the same position. It shows that BCP has the same optimizing effect as PEG [52], DIO [51], CN [53] on the crystallization of $MAPbI_{3-x}Cl_x$. As known, strong crystallization can improve charge carrier transport and the quality of $MAPbI_{3-x}Cl_x$, which implies that the devices have better performance (Fig. 4 (a)).

The compactness and effective coverage of $MAPbI_{3-x}Cl_x$ films enhance the performance of planer perovskite solar cells [9,10,33] by reducing leakage current [11,12], increasing recombination resistance [7,34] and improving the quality of the hole transport layer (HTL). Thus, it is crucial to fabricated compact $MAPbI_{3-x}Cl_x$ films with good coverage for application in $MAPbI_{3-x}Cl_x$ based perovskite solar cells. By utilizing BCP as additive in $MAPbI_{3-x}Cl_x$ based perovskite precursor solution, the holes on $MAPbI_{3-x}Cl_x$ film were reduced and the morphology of the $MAPbI_{3-x}Cl_x$ film was optimized (Fig. 3) with the increasing amount of BCP (from 0 μg/mL to 1200 μg/mL). Compared with Fig. 3, one can found that the excess BCP overflows into the grain boundaries on $MAPbI_{3-x}Cl_x$ film (Fig. 4 (b)) and reduces the pin-holes on the film. It indicates that the BCP is beneficial to the crystallization and morphology of the $MAPbI_{3-x}Cl_x$ film [50].

From the *J-V* curves in Fig. 4 (a), it can be seen that a moderate addition of BCP can enhance the *J-V* performance. The *J-V* curves display a comparison of device characteristics with and without BCP. The *J-V* performance did not increase until the amount of BCP was increased to 480 μg/mL. The specific photovoltaic parameters of a representative $MAPbI_{3-x}Cl_x$:BCP is shown in Table 1. Finally, the champion device with PCE of 16.25% was fabricated with an optimized amount of BCP (240 μg/mL) (Fig. 4 (a) and Table 1). There are three elementary reasons for the improved device performance as a result of the addition of the optimized amount of BCP. The first reason is that some ratios of BCP additive can improve the crystallization and quality of $MAPbI_{3-x}Cl_x$ films (Fig. 2 (c)), which is favourable for charge carrier transport.