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Effective and reproducible method for preparing low defects perovskite film toward highly photoelectric properties with large fill factor by shaping capping layer

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ABSTRACT

Recent development of perovskite solar cells have achieved great progress with power conversion efficiency reach to 22.1%. In this paper, we focus our attention on shaping perovskite capping layer (PCL) by adopting weak corrosive mixed anti-solvent to precisely control the capping layer thickness and crystallization. Ultra-dry gas flow was used for protecting perovskite film and inducing the formation of low defects perovskite crystal grain. The device performance is greatly enhanced after modifying the quality of $CH_3NH_3PbI_3$ films with suitable PCL thickness and crystalline grain. The power conversion efficiency was boosted from 8.79% to 18.25% for the champion cell with the fill factor as high as 80.91% measured under conditions of AM 1.5G, 100 mW/cm^2. It is expected that this method can be used as a general approach for boosting the perovskite solar cell efficiency with different type of precursor material (MA,FA group and diverse combination with each other), such as $MAPbX_3$, $FAPbX_3$ and $(FAPbI_3)_x(MAPbBr_3)_{1-x}$. Furthermore, the method exhibit good reproducibility and device stability due to high-quality perovskite films and the device of the best one will be not deteriorated with the PCE maintaining over 80% after 60 days.

1. Introduction

Organic-inorganic perovskite and its derivatives as a promising branch of solar cells have achieved rapid development (Snaith et al., 2012; Kanatzidis et al., 2014; Burschka et al., 2013; Zhou et al., 2014; Zhu et al., 2016; Li et al., 2016; Chen et al., 2015). In 2009, miyasaka research group successfully prepared a first perovskite solar cells (PSCs) using organic-inorganic hybrid material and got the power conversion efficiency of 3.8% (Miyasaka et al., 2012). Park reported Spiro-OMeTAD as HTM used in solid state organic/inorganic PSCs and achieved PCE of 9.7% to replace liquid-sensitized perovskite solar cells (Kim et al., 2012). Last year, seok's team used intramolecular exchange process (IEP) technique to induce perovskite to form crystals by PbI_2-DMSO react with FAI and got 20.1% power conversion efficiency. This record was kept for a period of time until the certified PCE of 22.1% was reported by KRICT (Im et al., 2014; Jeon et al., 2014; Kojima et al., 2009; Bi et al., 2016).

A great of research efforts contributed to increase PSC performance based on Lead organo-halide perovskite (Leijtens et al., 2015; Roesch et al., 2015; Shahbazi 2016; Zhang et al., 2015). In the early stage of PSCs development, snaith's work pointed that morphology is a critical issue (Snaith et al., 2014), then seok's group provided a morphology controlling method by anti-solvent engineering to form uniform and dense perovskite layers (Jeon et al., 2014). Besides, trap states at PCL surfaces, interstitial defects in perovskite crystal lattice, recombination between hole transporting layer (HTL) and electron transporting layer (ETL) etc. were extensively studied (Xiao et al., 2014; Yang et al., 2015; Emara et al., 2015; Ahn et al., 2015; Cohen et al., 2015; Kim et al., 2015). However, a critical factor that has a huge impact on the overall performance of PSCs is perovskite capping layer which was not given enough emphases (Roldan-Carmona et al., 2015).

In the mesoscopic $MAPbI_3$ PSCs, the mesoscopic TiO_2 layer are infiltrated by $MAPbI_3$ perovskite crystal. On top of the mesoscopic TiO_2 and under HTM layer, there is an overlayer (see Fig. 1) which

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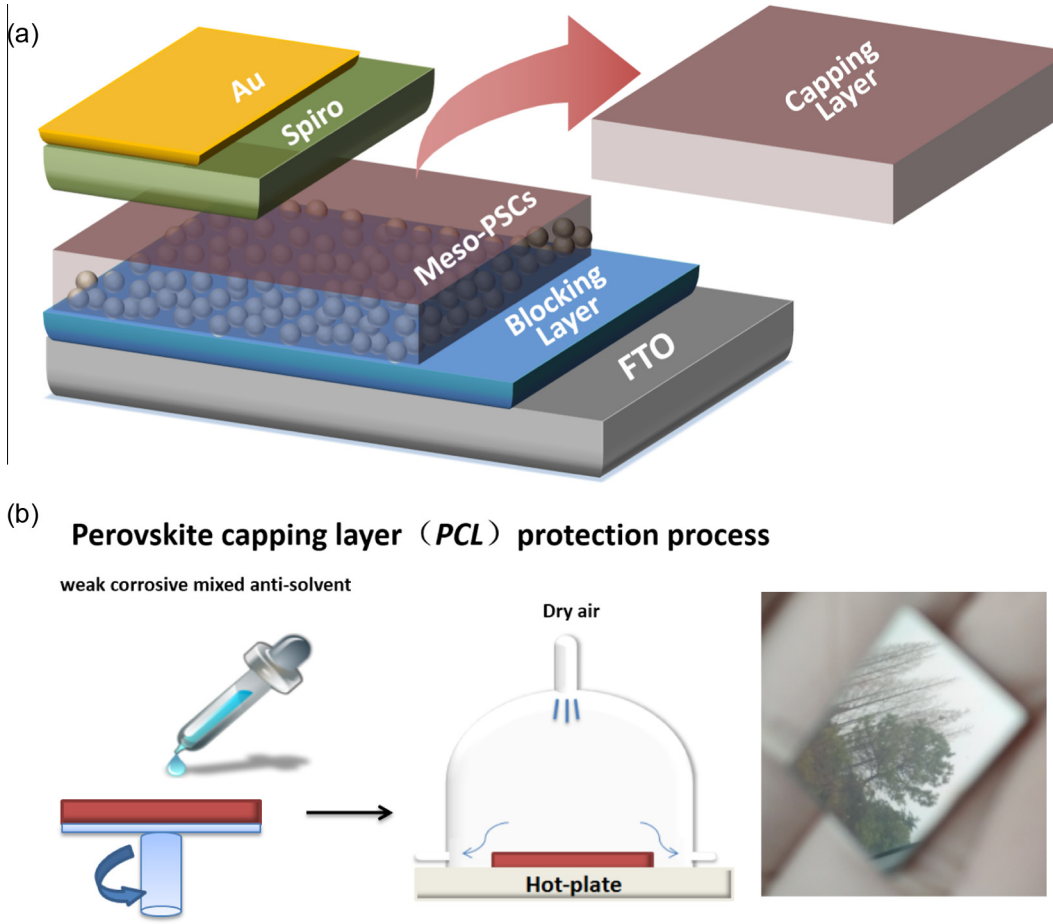

Fig. 1. (a) Device architecture of FTO/bl-TiO_2/meso-TiO_2 mixed perovskite/PCL/spiro/Au (b) Scheme of solvent engineering process for preparing perovskite solar cell capping layer with corrosive anti-solvent and gas flow protection.

was commonly referred to perovskite capping layer (abbreviated as PCL). The electron-hole pairs were generated by $MAPbI_3$ light-absorbing layer and then transported into mesoscopic TiO_2 layer and HTM layer respectively upon illumination of light. Although in the n-i-p structure devices, many factors would have an important impact on the performance, but the capping layer of perovskite itself determine the solar cell parameters of short circuit current, open circuit voltage and fill factor. A high quality PCL including the suitable capping layer thickness and excellent crystallinity which is an essential prerequisite for high performance PSCs (Yang et al., 2015).

In this article, we present high efficient methylammonium lead iodide PSCs (FTO/bl-TiO_2/meso-TiO_2 mixed perovskite/PCL/spiro/Au architectures). The PCL thickness was precisely controlled by changing the volume of weak corrosive mixed anti-solvent (8% acetonitrile in chlorobenzene, *volume ratio*). Ultra-dry gas flow was used for protecting perovskite film as well as inducing the formation of low defects perovskite crystal grain. A suitable thickness of capping layer can maximally absorb sunlight and at the same time will not block the absorption of light. This will guarantee more electron-hole pairs generation as well as reduce electron recombination (Liu et al., 2014). A perovskite solar cell with a thin PCL has relatively low performance mainly due to the recombination between TiO_2 and Spiro-MeOTAD (Bi et al., 2015). Under the premise of suitable thickness, PCL crystallization determines the further promotion of solar cell. In the conventional solvent engineering method, as far as we know there is no report about precisely controlling the thickness and crystallization of PCL by adding different doses of weak corrosive mixed anti-solvent under ultra-dry gas flow protection (Lin et al., 2015). Our results demonstrated that appropriate thickness of capping layer comprehensively improves the parameters of PSCs, boosting the power conversion efficiency from 8.79% to 18.25%, and average efficiency reached to 17.57% for the champion cell with the PCL thickness around 240 nm and good crystallinity grain. In addition, the as-prepared perovskite films with high fill factor have higher stability. The device without any encapsulation did not deteriorate with the PCE maintaining over 80% after 60 days. These results showed that by shaping PCL in PSCs can be used as an effective and easy approach toward high performance and stability perovskite solar cells.

2. Experimental

2.1. Materials

Lead (II) Iodide (99.99%, trace metals basis) [for Perovskite precursor] was purchased from TCI, CH_3NH_3I from Xi'an Polymer Light Technology Corp., TiO_2 (particle size: about 30 nm, crystalline phase: anatase) TiO_2 from dysol. DMF, chlorobenzene, lithium bis (trifluoromethylsulphonyl) imide (Li-TFSI) and 4-tert-butylpyridine (tBP) from Aldrich, and spiro-MeOTAD from Borun New Material Technology Co., Ltd. All chemicals were directly used without further purification. Patterned FTO-coated glass substrates with a sheet resistance of 15 ohm sq^{-1} were cleaned sequentially