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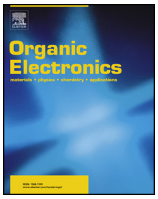

Enhanced photovoltaic performance and reduced hysteresis in perovskite-ICBA-based solar cells

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ABSTRACT

In this work, fullerene derivatives (ICBA and PCBM) are dissolved into perovskite precursors, and the corresponding perovskite solar cells are fabricated. Compared to PCBM, ICBA has better solubility in perovskite precursor solution (DMF). The added small amount of ICBA filled the vacancies at the grain boundaries of perovskite, and produced continuous pathways for electron extraction to enhance performance. Steady-state and time-resolved photoluminescence, together with the impedance measurements confirm the enhanced electron transporting property in perovskite-ICBA film. An excellent PCE of 18.14% is achieved in $CH_3NH_3PbI_{3-x}Cl_x$-ICBA-based solar cells with significantly suppressed hysteresis. Poor solubility of PCBM leads to a low concentration of PCBM in perovskite precursor, and results in a moderate PCE of 16.54% in device containing Perovskite-PCBM. By contrast, device based on pristine perovskite shows an inferior efficiency of 15.49% with large hysteresis. PSCs prepared from perovskite-ICBA with large area (1.12 cm^2) are also fabricated, exhibiting a PCE of 13.69%. Results demonstrate that the strategy of dissolving ICBA into perovskite precursor directly is an efficient and facile way to improve PSCs performance as well as to reduce hysteresis.

1. Introduction

The rapid development of the organic-inorganic hybrid perovskite solar cells (PSCs) receives widespread concerns in the solar cell community [1,2]. PSCs are attractive and compelling because of their low costs and high performances, in addition, the lead-halide perovskites have unique merits such as strong light absorption in a wide range, ambipolar transport property and long diffusion length of charge carriers [3–5]. In most cases, PSCs devices adopt a planar configuration, with the photo-active layer sandwiched between the electron transport layer (ETL, usually TiO_2) and the hole transport layer (HTL) [6,7]. By continuing efforts on improving perovskite morphology, exploring various additives and also by interfacial treatment, a certified high power conversion efficiency (PCE) of 22.1% has recently been reported [8–13], representing a remarkable achievement accomplished within ten years.

Although PSCs have achieved significant improvements, TiO_2-based planar architectures tend to suffer from severe hysteresis, that is, the *J-V* curves usually show deviations when scanning from different directions or at different scan speed [14,15]. On the other hand, the uncontrolled crystallization process of perovskite materials will create unwanted defects (pinholes and grain boundaries) [16–18]. In this regard, various additives have been adopted to precursor solution, in order to improve perovskite morphology and reduce or passivate defects. For example, benzoquinone is added into the precursor and the resulting perovskite films show improved morphology and crystal quality [13]. Polymers such as PMMA and PVA have also been incorporated as additives for the preparation of perovskite films respectively, the polymers are reported to control nucleation and crystal growth, leading to enhanced device performances and stability [19,20]. In 2014, Y. Shao and coworkers discovered that fullerenes deposited on the top of perovskite layer worked to reduce the trap density and eliminate photocurrent hysteresis [16]. Subsequently, perovskite-PCBM (PCBM: phenyl-C_{61}-butyric acid methyl ester) blends were prepared by independent groups, and the hybrid system was verified to reduce hysteresis and the recombination loss [17], as well as to improve the fill factor of an inverted bulk heterojunction device [21,22].

Although PCBM and its derivatives have been reported to fill the vacancies at the grain boundaries of perovskite, the solubility of PCBM in DMF is limited, thus the dissolved amount of PCBM in the perovskite precursor is quite small. In some cases, PCBM is dispersed, not dissolved in the precursor solution (DMF), as reflected by the Tindal Effect shown in Scheme S1. The dispersed PCBM particles are prone to aggregate, making the precursor solution unstable [17]. As another famous

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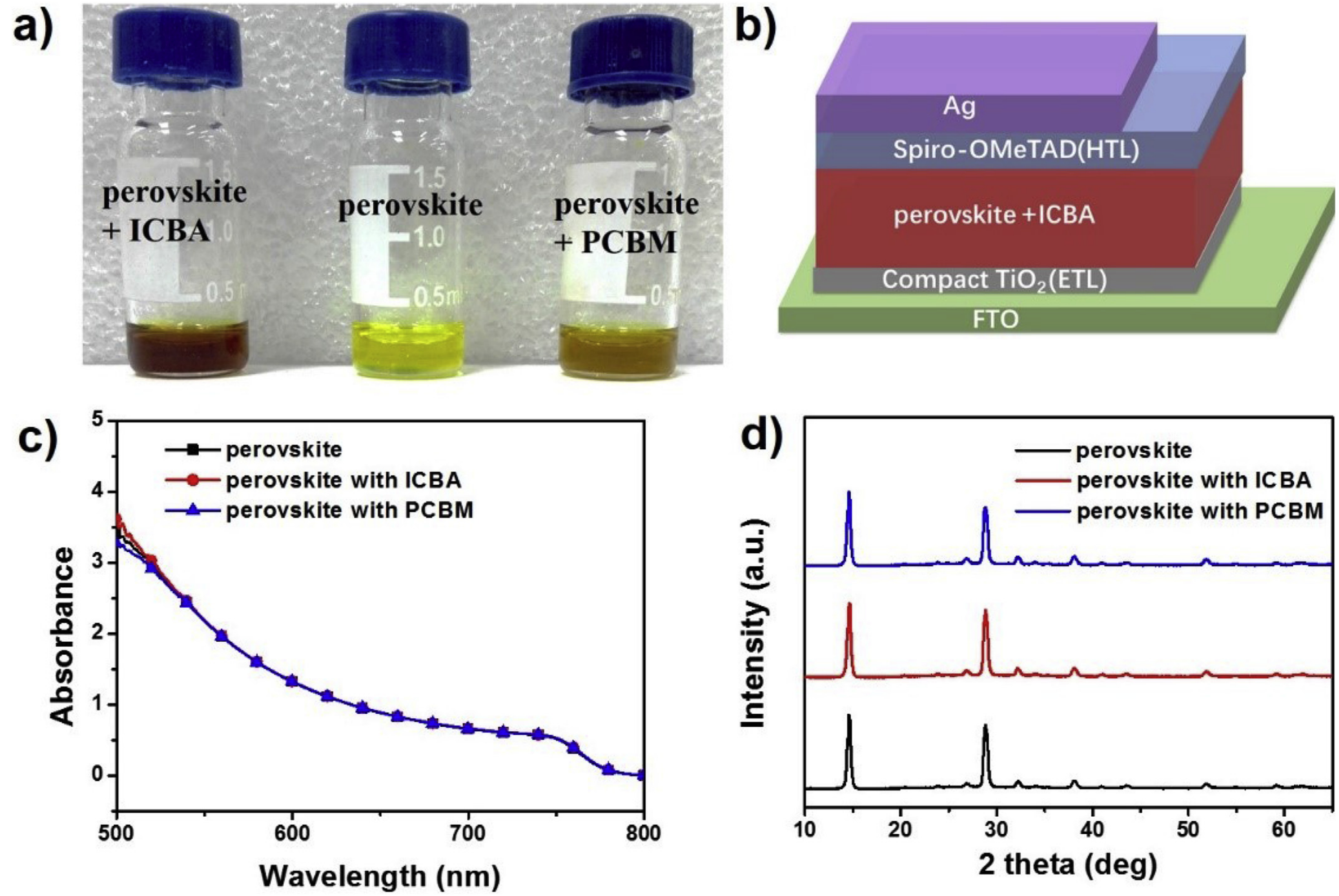

Fig. 1. A) Photos of different precursor solution, left: perovskite with ICBA, middle: pristine perovskite, right: perovskite with PCBM; b) Schematic representation of the device architecture in this work; c) UV-vis absorption spectra and d) XRD patterns of corresponding films prepared from perovskite, and perovskite mixed with ICBA and PCBM, respectively.

fullerene derivative, the indene-C_{60} biadduct (ICBA) is easy to prepare, furthermore, it has relatively better solubility in DMF than PCBM [23]. ICBA is similar in size with PCBM, and it also has high electron affinity. Moreover, the LUMO level of ICBA is about 0.17 eV higher than PCBM, which is closer to the conduction band of perovskite, yet with enough driving force for electron injection. Compared to PCBM, ICBA might be more favorable for extracting electrons from perovskite. Therefore, according to the reported effect of PCBM on perovskite materials [24], it is reasonable to expect that ICBA dissolved into the perovskite precursor may play similar roles to PCBM.

In this work, we prepare perovskite-ICBA blend by directly dissolving ICBA into perovskite precursor for the first time. For comparison, perovskite-PCBM blend and the pristine perovskite are also studied. Different from previous study on perovskite-PCBM systems [17,22], in which PCBM is dispersed in the precursor, in our cases, both ICBA and PCBM are directly dissolved into the precursor solution, and the perovskite-fullerene mixtures are then filtrated before use. Dissolving ICBA into perovskite precursor directly could avoid introducing other species or bringing about additional solvents into perovskite materials. Moreover, the dissolved solution is more stable than the dispersed systems. It turned out that the added ICBA helps to improve the film morphology, and facilitates electron transfer in perovskite-ICBA film. An excellent PCE of 18.14% is achieved in $CH_3NH_3PbI_{3-x}Cl_x$-ICBA-based solar cells, with an open-circuit voltage (V_{OC}) of 1088 mV, a short-circuit current density (J_{SC}) of 21.59 mA/cm^2, and fill factor (*FF*) of 0.77. Moreover, a PCE of 13.69% is obtained in large area (1.12 cm^2) PSCs prepared from perovskite-ICBA. In addition, the hysteresis in perovskite-ICBA-based device is significantly reduced. Under the same test condition, perovskite-PCBM-based PSCs shows a PCE of 16.54%, while device utilizing fullerene-free perovskite precursor exhibits a low PCE of 15.49% with large hysteresis.

2. Experimental section

2.1. Device fabrication

The TiO_2 compact layer (titanium precursor: 350 μL titanium (IV) isopropoxide and 25 μL HCl in 5 ml isopropanol), and the hole transport material precursor (72.5 mg Spiro-OMeTAD, 28.5 μL *t*BP and 17.5 μL Li-TSFI stock solution (520 mg/mL^1 in acetonitrile) in 1 mL chlorobenzene as dopants) were prepared as reported previously [25]. The primitive perovskite precursor solution was prepared according to literature procedures [26,27]. In detail, 0.44 mmol of PbI_2 and 0.44 mmol of $PbCl_2$ were mixed with 1.76 mmol of MAI in 1 mL of anhydrous DMF to get the precursor solution. The perovskite precursor (with ICBA or PCBM) was prepared in the following procedure. ICBA or PCBM was directly mixed into the perovskite solution and filtrated with a 0.45 μm size filter. To study the effect of the ICBA concentration, the primitive perovskite precursor and the precursor with ICBA in different concentrations (1.69 mg/ml, 0.85 mg/ml and 0.17 mg/ml) were prepared.

FTO-coated glass was sequentially washed by sonication using deionized water, ethanol and acetone. All the devices were fabricated using conventional “n-i-p” architecture (FTO/compact TiO_2/Perovskite/HTM/Ag). A compact layer of TiO_2 was deposited on FTO by spin-coating the titanium precursor at 5000 rpm for 60 s, followed by calcination on hotplate (500 °C, 60 min). Then the samples were