



The influence of perovskite precursor composition on the morphology and photovoltaic performance of mixed halide MAPbI_{3-x}Cl_x solar cells

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ABSTRACT

A set of various perovskite precursor formulations was investigated to elucidate correlations between precursor composition and the crystal structure, film morphology as well as photovoltaic activity of H₃CNH₃PbI_{3-x}Cl_x perovskite solar cells. Three precursor solutions in dimethylformamide (DMF) with defined ratios of lead(II) halide (PbI₂ and/or PbCl₂) and methylammonium halide (H₃CNH₃I (MAI) and H₃CNH₃Cl (MACl)) such as 1:3 (PbCl₂:MAI), 1:1:4 (PbI₂:PbCl₂:MAI) and 1:1:1 (PbI₂:MAI:MACl) were used to prepare solar cells in primarily ambient atmosphere. Processing the 1:3 (PbCl₂:MAI) solution in ambient atmosphere yielded perovskite films with rather non-uniform morphology and devices with moderate performance. Perovskite thin films prepared from the 1:1:4 (PbI₂:PbCl₂:MAI) and 1:1:1 (PbI₂:MAI:MACl) formulation showed nearly identical features, high crystallinity, large and compact micrometer-sized crystal domains, and good photovoltaic performance. This indicates that the overall ionic composition in the precursor solution is crucial for the perovskite formation, the source of these ions, however, appears nonrelevant. Furthermore, the effect of different electron transport layers (ETL), PCBM, *bis*-PCBM, and *N*-[4-(benzothiadiazol-4-yl)phenyl]-*N'*-(1-nonyldecyl)perylene-3,4,9,10-tetracarboxydimide (a-PTCDI) on the photovoltaic performance was analyzed. The highest hysteresis-free power conversion efficiency (PCE) was achieved with PCBM (12.8%) followed by a-PTCDI (8.4%) and *bis*-PCBM (6%). The degradation of MAPbI_{3-x}Cl_x based devices stored in nitrogen atmosphere was primarily revealed by a loss in fill factor.

1. Introduction

Organic-inorganic lead halide perovskites have emerged as high-performance photovoltaic materials and show great potential for next generation photovoltaic technology due to their high efficiency and low cost of fabrication (Burschka et al., 2013; Kim et al., 2012; Lee et al., 2012; M. Yang et al., 2015; W.S. Yang et al., 2015). These perovskites with appealing optoelectronic features are commonly prepared from organic halide and metal halide salts to form crystals in the perovskite ABX₃ structure comprising of organic and/or metal mono cation A, a divalent metal cation B, and halide anions X. Solution-processability and, compatibility with large-area deposition techniques, inexpensive base materials and desirable characteristics such as bandgap tunability, (Noh et al., 2013) high open-circuit voltage (V_{oc}), (Correa Baena et al., 2015) strong light absorption with high absorption coefficients (Kojima

et al., 2012; Löper et al., 2015) and high carrier mobility (Kagan et al., 1999; Mitzi et al., 1995) make this class of material very attractive for solar energy conversion. Additionally, ambipolar carrier transport within lead halide perovskites further highlights the unique excited state character of this special group of semiconductors (Etgar et al., 2012; Cui et al., 2017; Ke et al., 2015; Mei et al., 2014; Zhang et al., 2016).

The fabrication processes available for perovskites are robust and a myriad of approaches has been developed to deposit perovskite films. Perovskite solar cells can be processed using various techniques such as spin coating, (Lee et al., 2012) dip coating (Burschka et al., 2013), two-step interdiffusion (Xiao et al., 2014), chemical vapor deposition, (Chen et al., 2014) spray deposition, (Barrows et al., 2014) atomic layer deposition, (Sutherland et al., 2015) ink-jet printing (Wei et al., 2014) and thermal evaporation (Liu et al., 2013; Malinkiewicz et al., 2014)

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making them one of the most versatile photovoltaic (PV) technologies and potentially enables large flexibility in device design at low fabrication cost. A remarkable feature of the organic-inorganic halide perovskite system is the tunability of the crystal lattice dimensions through cation and/or anion variation, which defines the bandgap of these absorbers. Recent examples are the use of formamidinium cations (FA, $\text{HC}(\text{NH}_2)_2^+$) and of alternative halides. (Eperon et al., 2014a; Lee et al., 2015; Saliba et al., 2016; Yang et al., 2016) While pure perovskite compounds such as MAPbX_3 , FAPbX_3 and CsPbX_3 ($\text{MA} = \text{H}_3\text{CNH}_3^+$, $\text{X} = \text{I}^-$, or Br^-) showed numerous short comings, formulations based on mixed cations and halides yielded perovskite compounds with improved power conversion efficiency (PCE) as well as structural and thermal stability of the solar cell devices (Heo and Im, 2016; Jeon et al., 2015; Nie et al., 2015; Noh et al., 2013).

Understanding how to control the transformation from precursor solution into solid semiconductor is critical to produce high performance perovskite devices (Manser et al., 2016). Even in the relatively simple case of MAPbX_3 ($\text{X} = \text{I}^-$, Br^- , or Cl^-) precursor solutions, aside from the chosen halide (Lee et al., 2012; Stranks et al., 2013; Zhao and Zhu, 2014) variations in the solvent (Jeon et al., 2014; Kim et al., 2014), stoichiometry of the components (Manser et al., 2015; M. Yang et al., 2015; W.S. Yang et al., 2015), processing atmosphere (Ko et al., 2015; You et al., 2014), annealing temperature and time (Eperon et al., 2014b; Saliba et al., 2014) can affect the morphology and optoelectronic properties of the resulting film distinctively. Hence, it is of great significance to explore new processes for low-temperature fabrication of organic-inorganic perovskites and provide a better understanding of some fundamental physical and chemical properties of these materials. To date all high-efficiency perovskite solar cells reported make use of formulations based on mixed cations and halides (Jeon et al., 2015).

Another common feature of such high-performance perovskite-based solar cells is the integration of mesoscopic metal oxide interlayers such as Al_2O_3 , TiO_2 or ZrO_2 with an expense of high-temperature sintering process. Such a high temperature processes, however, are usually not compatible with low-cost, lightweight and flexible plastic substrates (Docampo et al., 2013; Roldán-Carmona et al., 2014; Sun et al., 2014) and multi-junction device architectures (Bailey and McGehee, 2012). Substitution of the metal oxide layers by organic semiconductors can help to overcome such obstacles and to simplify the fabrication of devices.

To enhance exciton separation, charge transportation and collection, the deposition of a conformal and chemically inert electron transport layer (ETL) on top of the perovskite film to complement the underlying hole transport layer appears essential for the fabrication of high-efficient planar heterojunction perovskite solar cells (Yin et al., 2016). Reports on polymer-based bulk heterojunction solar cells showed the use of *bis*-PCBM instead of PCBM can lead to an increase in V_{oc} , which is attributed to its significant higher lowest unoccupied molecular orbital (LUMO) level. (Han et al., 2016; He and Li, 2011; Lenes et al., 2008). Perylenetetracarboxylic diimides (PTCDIs), originally developed as pigments with high resistance to degradation, are used as non-fullerene acceptors due to their n-type properties and the vast possibilities of structural modifications to tune their optoelectronic and morphological features (Huang et al., 2011; Zhan et al., 2011). Kaltenbrunner et al. (2015), reported efficient planar heterojunction $\text{MAPbI}_{3-x}\text{Cl}_x$ solar cells using *N,N'*-dimethyl-3,4,9,10-tetracarboxylic perylene diimide, thermally deposited in vacuum, as an electron transporting material. In addition to this, the stability of perovskite based devices remains an open question and perhaps will determine the fate of these promising materials for technological application in the long run.

In this work, we investigate the straightforward fabrication of planar p-i-n heterojunction perovskite solar cells, (ITO/PEDOT:PSS/perovskite/ETL/Al), excluding high temperature processing steps and using almost exclusively solution-processing techniques in ambient atmosphere. As a first objective, three different $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite

precursor compositions, 1:3 (PbCl_2 :MAI), 1:1:1 (PbI_2 :MAI:MAcI) and 1:1:4 (PbI_2 : PbCl_2 :MAI) dissolved in dimethylformamide (DMF), were investigated regarding their conversion into perovskite thin films in ambient atmosphere. Using identical processing procedures the emphasis of the study is on the composition of the three precursors formulations. While 1:1:4 and 1:1:1 use in parts different base components, the overall composition of ions in the two precursor formulations is identical ($\text{Pb}^{2+}:\text{MA}^+:\text{I}^-:\text{Cl}^- = 1:2:3:1$). In the precursor formulation 1:3 ($\text{Pb}^{2+}:\text{MA}^+:\text{I}^-:\text{Cl}^- = 1:3:3:2$) the content of the excessive MAcI is twice as high. The morphology and crystallinity of the obtained perovskite films were investigated by means of scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD), respectively. The solar cell performance was investigated by current density-voltage and external quantum efficient measurements. The processing of 1:3 (PbCl_2 :MAI) in ambient air resulted in poor film morphology and was found to be detrimental to the perovskite crystal structure. In contrast we found substantial better and nearly identical morphology and crystallinity, as well as performance in the perovskite films obtained from the 1:1:1 (PbI_2 :MAI:MAcI) and the 1:1:4 (PbI_2 : PbCl_2 :MAI) precursor formulations. Another critical element in our device layout was the deposition of an inert electron-transporting layer (ETL). We probed three electron-transport materials, *bis*-PCBM, PCBM and an amorphous PTCDI derivative (a-PTCDI) simply deposited from solution at room temperature. The best performing planar perovskite solar cells employing PCBM, a-PTCDI and *bis*-PCBM as electron transport materials achieved power conversion efficiency of 12.8, 8.4 and 6%, respectively. Solar cells which were obtained from the 1:1:1 (PbI_2 :MAI:MAcI) formulation showed good shelf stability in nitrogen-filled glove box.

2. Experimental

2.1. Materials

Chemicals and solvents were purchased from commercial suppliers and used as received, if not stated otherwise. Pre-patterned indium doped tin oxide (ITO) coated glass ($15 \text{ Ohm}/\text{cm}^2$), PbI_2 (99.9%, Sigma Aldrich), PbCl_2 (99.9%, Sigma Aldrich), dimethylformamide (DMF, anhydrous, Sigma Aldrich), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Clevis PH 1000), Zonyl®FS-300 fluorosurfactant (40% in H_2O , Fluka), dimethyl sulfoxide (DMSO, AnalR, VWR Chemicals), [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM; SolenneBV), *bis*-adduct of phenyl- C_{61} -butyric acid methyl ester (mixtures of isomers, *bis*-PCBM, SolenneBV), chlorobenzene (GPR, VWR Chemicals), chloroform (AnalR, VWR Chemicals), isopropanol (AnalR, Fisher Chemicals) and methylammonium chloride (MAcI, MERCK) were used as received. Methylamine (33 wt%, in absolute ethanol, Sigma Aldrich), hydroiodic acid (57 wt%, aqueous, Riedel de Haën), diethyl ether (VWR Chemicals), and ethanol (absolute, MERCK) were used to synthesize and purify methylammonium iodide (MAI) according to literature (Burschka et al., 2013). *N*-[4-(benzothiadiazol-4-yl)phenyl]-*N'*-(1-nonyldecyl)perylene-3,4,9,10-tetracarboxydimide (IUPAC: (2-[4-(2-(1,3-benzothiadiazol-4-yl)phenyl]-9-(1-nonyldecyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetrone; registry number 1417610-38-8) an amorphous PTCDI derivative, in here abbreviated as a-PTCDI, was synthesized according to literature (Langhals et al., 2012).

2.2. Perovskite precursor solutions

$\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite precursor formulations of 0.8 M concentration were prepared by dissolving defined molar ratios of lead halides and methylammonium halides, 1:3 (PbCl_2 :MAI), 1:1:4 (PbI_2 : PbCl_2 :MAI) and 1:1:1 (PbI_2 :MAI:MAcI), in DMF. To ensure a complete dissolution the mixtures were stirred overnight at room temperature. The solutions were filtered through a PTFE syringe filter (0.45 μm) before use.

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