Photovoltaic Effect of 2D Homologous Perovskites

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ABSTRACT

The controlled growth of mixed dimensional perovskite structures, $(C_6H_5CH_2NH_2)(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$, through the introduction of CH_3NH_3I molecule vapor into the two-dimensional perovskite $C_6H_5CH_2NH_3PbI_4$ structure and its application in photovoltaic devices is reported. The dimensionality of $(C_6H_5CH_2NH_2)(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ is controlled using the exposure time to the CH_3NH_3I vapor on the $C_6H_5CH_2NH_3PbI_4$ perovskite film. As the stacking of the lead iodide lattice increases, the crystallographic planes of the inorganic perovskite compound exhibit vertical growth in order to facilitate efficient charge transport. Furthermore, the devices have a smaller band gap, which offers broader absorption and the potential to increase the photocurrent density in the solar cell. As a result, the photovoltaic device based on the $(C_6H_5CH_2NH_2)(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ perovskite exhibits a power conversion efficiency of 5.43% with a short circuit current density of 14.49 mA cm^{-2}, an open circuit voltage of 0.85 V, and a fill factor of 44.30 for the best power conversion efficiency under AM 1.5G solar irradiation (100 mW cm^{-2}), which is significantly higher than the 0.34% of the pure two-dimensional BAPbI$_4$ perovskite-based solar cell.

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1. Introduction

The organic-inorganic hybrid perovskite $CH_3NH_3PbI_3$ is a potential material for cost-effective photovoltaic applications. It has remarkable solar conversion efficiency that surpasses the conventional dye-sensitized solar cells, amorphous silicon solar cells, and other promising photovoltaic technologies. Its primary advantages as a light absorber for solar cell devices are ascribed to its potential for defect-free crystalline film formation at low temperatures with a solution process [1], its high optical absorption coefficient ($\alpha = 10^4$–10^5 cm^{-1} for $hv > 1.7$ eV) [2], its long electron and hole diffusion length (> 1 μm for $CH_3NH_3PbI_3$$_xCl_x$ and > 175 μm for single crystal $CH_3NH_3PbI_3$) [3,4], and its low exciton binding energy (50 meV) [5]. These unique properties have increased the power conversion efficiency of perovskite photo-voltaics from 3.8% in 2009 [6] to more than 20% in 2014 [7,8]. Recently, the $CH_3NH_3PbI_3$ perovskite was applied to perovskite/silicon tandem cells due to its steep absorption edge and tunable band gap energies (1.48–2.23 eV), which demonstrate its potential for efficiencies beyond 30% [9–11].

Although the progress in device efficiencies has been remarkable, issues of hysteresis [12–14] and material instability [15,16] are

of significant interest. Because three-dimensional (3D) perovskites (e.g. $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$) have a highly ionic characteristic, they are very sensitive to ambient conditions, particularly moisture and oxygen, which have been found to detrimentally decompose the perovskite crystal structure.

However, two-dimensional (2D) perovskites, which constitute bulkier organic molecules in place of $CH_3NH_3^+$ in $CH_3NH_3PbI_3$, exhibit more resistance to humidity than the 3D analogues. It has been reported that 2D perovskite structures are very stable because the excitons in the 2D structure have a high binding energy (0.36 eV), even at room temperature [17,18]. The charge transfer in these structures occurs with two transitions, from the valence band and the nonbonding state of the inorganic layer to the lowest occupied molecular orbitals of the organic layer. This characteristic significantly affects the excitonic process, which contributes to the solar cell device efficiency. However, 2D perovskites have been hindered as light absorbers due to their higher band gap, low absorption coefficient, and poor carrier transport. In perovskites that utilize M-I frameworks as the inorganic component, the size and functionality of the organic cation has been demonstrated to significantly influence the dimensionality and connectivity of the inorganic lattice. Small-sized organic cations such as methylammonium and formamidinium result in 3D hybrid perovskites, while slightly larger organic cations form 2D layered perovskites. Therefore, although 2D

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perovskites exhibit interesting photoluminescence properties, the larger organic cations decrease the carrier mobility due to the disconnectivity between the $[MI_4]^{1-}$ layers.

Recently, it was reported that mixed dimensional perovskites can overcome these disadvantages. For example, the mixed perovskite with 2D and 3D materials can continuously tune the band gap between the 2D and 3D perovskites and combine the enhanced stability of the 2D perovskite with the excellent optical properties of the 3D perovskites, which enables the fabrication of very stable, highly efficient solar cells. Karunadasa et al. [19] demonstrated that a planar solar cell with a $(C_6H_5C_2H_4NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$ layered perovskite yielded a power conversion efficiency of 4.73%. Koh et al. [20] reported the controlled growth of nanostructured mixed dimensional perovskite, i.e. $(IC_2H_4NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$, using the sequential deposition method. They achieved an overall power conversion efficiency of 9% with this mixed dimensionality perovskite system. However, these methods are very complicated and require specific processes when they are transformed from the solution into a film. Therefore, a new, facile method of fabricating highly qualified mixed dimensional perovskites should be developed.

In this paper, the research is focused on the instability of the 3D perovskite, while complementary studies of the physical and optoelectrical properties of the 2D perovskites enable the identification of the ideal perovskite structure for obtaining high efficiency photovoltaic devices. For this reason, the platform of the dimensionally tuned 2D perovskite $C_6H_5CH_2NH_3PbI_4$ ($BAPbI_4$) structure with the 3D perovskite $CH_3NH_3PbI_3$ ($MAPbI_3$) is investigated using a reaction predeposited $BAPbI_4$ thin film with hot MAI gas in the perovskite structure, which results in the mixed dimensional perovskite structure of $(C_6H_5CH_2NH_2)(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$. This approach differs to the previously reported method in that it is very simple and the reproducible perovskite structure can be obtained easily. The increased dimensional perovskite exhibits a smaller band gap as a result of the improved lamination of the inorganic layer, which enables the potential for a higher photocurrent density and fill factor in the solar cell device. The efficiency of the solar cell prepared with the dimensionally tuned perovskite demonstrates the highest power conversion efficiency of 5.43%, which is significantly higher than that of the pure 2D $BAPbI_4$-based solar cell, and it has superior stability compared with the cell prepared using 3D $MAPbI_3$. As a result, the mixed dimensional perovskite system can be used as a foundation to achieve next-generation high efficiency solar cells.

2. Experimental Section

2.1. 2D and 3D perovskite preparation

The 2D and 3D perovskites were prepared through changing the organic molecules between the inorganic layer and the organic spacer molecules, i.e. benzylamine and methylammonium for the 2D and 3D perovskites, respectively. A 100 mL two-necked round-bottom flask was charged with 10 mL of HI (57% aq., 1.5% H_3PO_2) and a stir bar. The solution was degassed with nitrogen for 1 min, and the flask was kept in nitrogen for the duration of the experiment. The flask was heated to 100 °C in an oil bath while stirring, at which point lead iodide (PbI_2, 1.383 g, 3 mmol) was added and then the mixture was stirred vigorously to dissolve the lead iodide; this resulted in a translucent bright yellow solution. The flask was heated to 120 °C, at which point benzylamine hydrochloride (0.287 g, 6 mmol) and methylamine hydrochloride (0.405 g, 6 mmol) were added according to the dimensional perovskite. After adding the organic molecules, the heat was turned off, the flask was removed, and it was allowed to cool to room temperature. Once cool, the solution was filtered and then dried at 50 °C for 24 h.

2.2. Solar cell device fabrication

The N-type TiO_2 layer was formed using the following method. A 50 nm TiO_2 blocking layer (TiO_2 BL) was deposited on the FTO substrate via spin coating (2000 rpm, 30 s) a mildly acidic solution of titanium isopropoxide (TTIP) in ethanol (350 μL TTIP in 5 mL EtOH containing 0.013 M HCl), and then the sintering process was conducted at 550 °C for 30 min. A mesoporous TiO_2 layer was spin-coated on the TiO_2 compact layer with a diluted TiO_2 paste (DYESOL-30NRD) with ethanol at a ratio of 1:3.5 w/w at 500 rpm for 5 s, 3000 rpm for 10 s, and 6000 rpm for 30 s. The substrate was further treated with 20 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, rinsed with deionized water and ethanol, and then sintered at 500 °C for 30 min. Next, 30 wt% $BAPbI_4$ perovskites were dissolved in the DMF solvent. The solution was spin-coated on the N-type TiO_2 layer at 4000 rpm for 30 s followed by an annealing process at 100 °C for 1 min in order to eliminate residual solvents. Subsequently, the lab-made CH_3NH_3I powder was dispersed around the cooled $BAPbI_4$ film on a hot plate as described in the literature [21]. The sample was covered with a glass container and annealed at 160 °C from 30 s to 7 min.

To fabricate the 3D $CH_3NH_3PbI_3$ peovskite device, a 40 wt% precursor solution of PbI_2 and MAI (molar ratio 1:1) in DMF was made and then, spin-coated on the TiO_2 mesoporous layer at 6000 rpm for 30 s. The film was annealed at 100 °C for 10 min. The hole transporting layer was prepared according to the literature [22]. A solution for the spiro-MeOTAD coating was prepared through dissolving 72.3 mg spiro-MeOTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis(trifluoromethanesulfony) imide solution (520 mg Li-TSFI in 1 mL acetonitrile) were added. The spiro-MeOTAD was deposited on the perovskite layer at 4000 rpm for 30 s. For the counter electrode, a gold layer of 800 Å was deposited on the perovskite layer with the thermal evaporation at 1 Å s^{-1}.

2.3. Device performance measurement

The photocurrent (J_{sc}) and photovoltage (V_{oc}) of the solar cell were measured with an active area of 0.2 cm^2 using simulated solar light at AM 1.5G produced by a 1000 W xenon lamp (Oriel, 91193). Its irradiant power was adjusted according to a Si reference solar cell (Fraunhofer Institute for Solar Energy System: Mono-Si + KG filter) to have approximately one-sun light intensity (100 mW/cm^2). The incident photon-to-current efficiency (IPCE) was measured using a system designed using the photovoltaic measurement. A 12 W halogen lamp was applied as a light source for the monochromatic beam. For its calibration, a silicon photodiode (NIST-calibrated photodiode G425) was used. The IPCE data were obtained at a low chopping speed of 5 Hz, and the quantum efficiency was detected using a lock-in amplifier. The electrochemical impedance spectroscopy (EIS) data were obtained under one sun illumination using a potentiostat (Solartron 1287) equipped with a frequency response analyzer (Solartron 1260) under a frequency ranging from 10^{-2} to 10^6 Hz.

The intensity modulated photovoltage spectroscopy (IMVS) and intensity modulated photocurrent spectroscopy (IMPS) measurements were performed on a ZAHNER CIMPS system. The LED was operated using a potentiostatic feedback loop to control the stationary DC voltage and a concurrent sinusoidal modulated AC voltage. The AC amplitude was determined from 10% of the stationary DC value. The transfer functions of IMPS and IMVS were